BIOLOGICAL AVAILABILITY OF NITROGEN IN CERTAIN CONDENSATION PRODUCTS OF THE REACTION OF UREA WITH FORMALDEHYDE

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INTRODUCTION

The three factors which largely determine the efficiency of a given nitrogenous fertilizer material are the percent of nitrogen that becomes available in a reasonable length of time, the resistance to luxury consumption of nitrogen by plants in early periods of the fertilizer cycle, and the resistance to leaching losses. All together determine the characteristics of a time-availability curve for a material.

Water-soluble fertilizer nitrogen has two characteristics which affect its efficiency. There is luxury consumption of nitrogen by plants in the early stages and nitrogen deficiency in later stages as a result of this early massive uptake plus possible leaching. Thus, economical fertilization of crops in a manner that provides a continuous supply of nitrogen becomes a real problem, especially on light sandy soils.

These disadvantages of readily soluble nitrogen have led research workers to seek more desirable sources. An ideal material would be one in which the nitrogen becomes available over a relatively long period of time yet at a rate high enough to supply plant needs. Such a material would reduce luxury consumption, leaching losses, and retard the advent of nitrogen deficiency.

One line of search for a more desirable fertilizer source of nitrogen has been a study of urea-formaldehyde condensation products. Under certain conditions urea reacts with formaldehyde, forming relatively insoluble compounds which release their nitrogen slowly in the soil. They can be made to vary in solubility depending upon the conditions under which they are produced. Factors such as pH, reaction time, temperature, and concentration of reactants are known to affect the solubility of the final product.

Under the proper conditions formaldehyde and urea react to give nearly quantitative yields of dimethylolurea. The nature of the reactions involved is not fully understood but it has been postulated that methyleneureas are formed as intermediate products through the loss of water. These methyleneureas polymerize irreversibly.

This investigation involved a study of the availability of the nitrogen in certain of these synthetic nitrogen carriers with special emphasis on the availability of the insoluble nitrogen produced by the use of N-dure[1] solution in the manufacture of mixed fertilizers. The rate at which the relatively insoluble materials so formed release their nitrogen was determined by a study of their nitrification rates in the laboratory, and by pot tests in the greenhouse using Lakeland fine sand.

The primary objectives of this study were as follows: (1) to determine the rate of nitrification of these materials in Lakeland fine sand at two pH levels in the laboratory under controlled conditions of temperature and moisture; (2) to determine the nitrogen uptake in the greenhouse by oats and millet from Lakeland fine sand to which various amounts of the materials had been added.

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[1] N-dure is a solution containing 59 percent formaldehyde and 26 percent urea manufactured by Allied Chemical Corporation.

The experimental procedures employed were designed to screen numerous materials, and to indicate those with complex reactions requiring further studies at some future date. Ammonification studies were not included because at this stage of the screening the tedious cold asperation procedure of ammonia determination was not thought to be justified. Hot distillation procedures are not acceptable for materials of unknown decomposition characteristics.

LITERATURE REVIEW

The present interest in urea-formaldehyde compounds as nitrogenous fertilizers in the United States had its beginning about 1946 in the Bureau of Plant Industry, Soils and Agricultural Engineering, U. S. Department of Agriculture, Beltsville, Maryland. Most of this early work [49] was conducted by Clark, Yee, Love, Armiger and Boyd, who published on the subject during 1946-1951.

Yee and Love [51] prepared a series of nine samples of urea-formaldehyde material. The mole ratios of urea to formaldehyde (subsequently referred to as U/F ratios) of the reactants ranged from 0.75 to 7.5. However, the U/F ratios of the products were much narrower, ranging from 0.88 to 2.0. The water solubility of these products was found to increase with an increase in U/F ratio. The availability of the nitrogen in these products was assessed by determining their rates of nitrification at 30°C. It was found that the nitrification rates increased with an increase in the U/F ratio. The products with U/F ratios of 0.88 and 1.03 nitrified too slowly for practical fertilizer use. Most promising of the products as a source of slowly available nitrogen were those with U/F ratios ranging from 1.18 to 1.36. The materials nitrified slowly at fairly constant rates for about three months and from then on at reduced rates. However, the initial activity of these materials was low. The availability of the nitrogen in the urea-formaldehyde products was found to be roughly proportional to their solubility in water.

Clark, et al. [11, 12] produced urea-formaldehyde reaction products suitable for fertilizer use that contained 36 percent or more of nitrogen and having varying rates of availability. These products were produced from both dilute and concentrated solutions having molar U/F ratios ranging from 0.75 to 7.5 under various conditions of acidity, reaction temperature, and time. They found that the nitrogen availability patterns of such products were largely determined by their U/F ratios and nitrogen solubility indexes--the lower the U/F ratio and solubility index, the lower the rate of availability of nitrogen. It was found that the solubilities of the urea-formaldehyde products produced increased with time. Therefore, relative solubilities were established by adopting a procedure whereby the amount of nitrogen dissolved from a one gram sample by 400 ml. of distilled water in 24 hours at 30°C. was determined. The products obtained by the reaction of urea and formaldehyde were found to be affected by the U/F ratio, pH, temperature, reaction time, concentration of solution, and possibly other factors. From their experiment it was concluded that under any given set of conditions the products produced were mixtures of at least two and probably several different compounds.

Winsor [46] later reported results similar to those of Clark et al. [11, 12] with respect to the solubility of urea-formaldehyde products as influenced by the U/F ratio.

Clark et al. [8, 13] reported that the reaction between urea and formaldehyde compounds appeared to progress through methylol urea formation to increasingly more complex polymethylene urea compounds.

They also stated that the neutralization of the reaction mixture at the proper stage largely inhibits completion of the reaction to excessively insoluble materials and stabilizes the product against subsequent heat treatment.

Kolterman [29] reported findings similar to those of Clark and his co-workers and stated that ureaform[1] is made up principally of methylene urea ranging from small readily soluble molecules to long chain insoluble molecules which breakdown differentially in the soil, providing gradual release of nitrogen to plants. As a result, urea-formaldehyde products vary from those having little or no fertilizer value to those which approach an ideal nitrogen availability pattern. He also stated that the commercial manufacture of high quality ureaform is very complex and requires critical process control.

Clark [9] reported that the most promising urea-formaldehyde products were those containing 24 to 28 parts of urea by weight for each 10 parts of formaldehyde.

Microbiological studies of urea-formaldehyde preparations were made by Fuller and Clark [21] who found that these preparations, under the proper conditions, are hydrolyzed to ammonia by enzymes produced by microorganisms. There was no appreciable amount of ammonia produced in the absence of microorganisms. No apparent toxicity to soil flora occurred when these preparations were applied at rates equivalent to 1 percent of the soil. Nitrification proceeded satisfactorily when these urea-formaldehyde preparations were applied to the soil at rates considerably above those likely for practical usage in the field.

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[1] A general term applied to urea-formaldehyde fertilizer materials.

Several other workers [10, 20, 31, 34, 35, 39, 44, 47, 48] have conducted nitrification studies on urea-formaldehyde products and in most cases similar results were obtained, but certain of the results obtained appear to be conflicting. Some disagreement might be expected since most of the experiments were conducted on slightly different urea-formaldehyde compounds and on different soils under various conditions. In general, it was found that the rate of decomposition of these compounds was affected by such factors as soil type, soil pH, and the characteristics of the particular compound being tested, which was the result of conditions under which it was produced. Long and Winsor [34] found that urea-formaldehyde compounds prepared by reaction under alkaline conditions, followed by a brief acid treatment, were more readily decomposed in the soil than were similar products prepared under acid conditions alone. Winsor and Long [47] also showed that the rates of conversion of urea-formaldehyde products into inorganic forms of nitrogen increased with decreasing soil pH values with the highest rates of nitrification occurring in soils having an initial pH value of 5.5 to 6.0.

Kralovec and Morgan [31], in their study of the nitrification rates of urea-formaldehyde compounds containing about 38 percent nitrogen, of which about 75 percent was in the slowly available water-insoluble form, found that the average rate of nitrification amounted to 55 to 60 percent within six months and was affected by the soil type, soil pH, and general nutrient status of the soil. They state that these compounds appear to be ideally suited for long-season crops such as turf and greenhouse plants.

Owen et al. [39] obtained relatively high percentages of mineralization (71.4 percent) of products prepared at low temperature, irrespective of their water-soluble nitrogen content.

Davis [18] reported that the neutral potassium permanganate method employed to determine the availability of nitrogen in natural organics is not applicable to urea-formaldehyde compounds. Morgan and Kralovec [36] described a simple and rapid method for predicting the agronomic value of urea-formaldehyde polymers. They stated that the method is superior to existing methods and shows close correlation with time-consuming soil nitrification tests. The procedure requires the determination of nitrogen insoluble in cold water, and of nitrogen insoluble in hot buffered phosphate solution. The percentage of cold-water insoluble nitrogen that dissolves in the hot buffered solution is an index of the availability of the cold-water insoluble nitrogen.

Armiger et al. [4, 5] did a considerable amount of work on the evaluation of eleven urea-formaldehyde preparations as sources of slowly available nitrogen for Bermudagrass and perennial ryegrass.

This experiment was conducted in the greenhouse with two soils; namely, Chillium subsoil (8 to 16 inches) with a pH of 4.8, high sand content, and low fertility, and Evesboro loamy sand (0 to 8 inches) also with a pH of 4.8 and low fertility. Solubility determinations and nitrification studies had previously been made on the eleven urea-formaldehyde preparations used in this experiment. The mole ratios (U/F) of these materials ranged from 1.03 to 1.36. Milorganite (an activated sewage sludge) and ammonium sulfate were used for comparison in the Bermudagrass experiment while Uramon (fertilizer grade of urea), Milorganite, and cottonseed meal were used for comparison in the perennial ryegrass experiment.

In the Bermudagrass experiment the crop responded much more rapidly to applications of ammonium sulfate and Milorganite than to any of the urea-formaldehyde materials. However, the nitrogen of the urea-formaldehyde materials was available to the crop over a much longer period of time due to their initially low but extended rate of nitrogen availability. The ureaform materials seemed to stimulate greater root and crown development than did the ammonium sulfate. The added nitrogen recovered in the clippings in 315 days showed that Milorganite and ammonium sulfate supplied 69 and 97 percent respectively of their total contribution of nitrogen to the grasses in the first 64 days, whereas the ureaform materials supplied only 32 to 57 percent of the total nitrogen added in the same period.

A portion of the perennial ryegrass experiment was conducted on cropped Evesboro soil. Three of the ureaform materials (ratios of 1.12, 1.19, and 1.25) were used in combination with Uramon. In the mixtures, one-third of the nitrogen was supplied by Uramon and two-thirds by the ureaform materials. The results obtained indicated that one-third of the nitrogen supplied by a readily available source was too high.
A ureaform material with 10 to 20 percent of the nitrogen from a readily

available source probably would have given a better growth curve. It was found that 81 percent of the recovered nitrogen was found in the clippings of the Uramon-treated plants during the first 46 days. The nitrogen recovery in the clippings of the plants treated with ureaform with a mole ratio of 1.25 recovered only 27 percent during the same period. However, during the latter part of the experiment (111 to 132 days) these positions were reversed, with the ureaform (ratio 1.25) showing a recovery of 25 percent of its total recovery in comparison to 3 percent for Uramon. The total yield was slightly higher from ureaform materials than from readily available sources of nitrogen and the availability pattern of the ureaform materials was far superior to Milorganite and Uramon. Two of the ureaform materials (numbers 475 and 476) were outstanding in that they yielded dry matter relatively high in nitrogen over longer periods of time than any of the others. These two materials had higher secondary solubility values than the other ureaform preparations.

Musser et al. [38] conducted experiments similar to those of Armiger et al. and obtained comparable results. They concluded that ureaform products of the ratios tested were satisfactory sources of slowly available nitrogen for use on turf, and that they could be used advantageously to replace or supplement supplies of natural organic nitrogenous fertilizers.

Numerous other workers [2, 23, 24, 33, 37, 50] have reported similar work on turfgrasses.

Volk [45] in studying the comparative efficiency of various nitrogen carriers, found that the total nitrogen uptake by oats from a light sandy soil to which Duramene (a urea-wood waste product carrying water-insoluble nitrogen) was added was about 85 percent of the total uptake of nitrogen where cottonseed meal was used. Under leaching tests, 15 to 20 percent of the nitrogen was removed from Duramene while 70 percent of the nitrogen from calcium nitrate was lost.

Scarsbrook [41] found that urea-formaldehyde products with a nitrogen availability index[1] of 20 was too low for cotton and corn. Formulations with availability indexes of 49 and 57, however, proved to be more promising.

Ureaform [3] has shown promise also as a source of nitrogen for tobacco. The best crop value (yield and grade) was obtained with a mixture of 25 percent ureaform and 75 percent cottonseed meal.

With the advent of the encouraging results obtained with the ureaform materials as a source of slowly soluble nitrogen, numerous workers [1, 7, 14, 15, 16, 17, 22, 25, 27, 28, 30, 32, 40, 42] obtained patents on various methods of producing these materials. In general, the differences in the methods were those of reaction time, pH, temperature, U/F ratios, and concentration of the urea and formaldehyde solutions used. These differences produced urea-formaldehyde materials of various percentages of water-insoluble nitrogen. The total nitrogen was usually about 38 percent, of which the water-insoluble nitrogen ranged from about 34 percent to 68 percent.

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[1] The availability index is a measure of the nitrification rate of urea-formaldehyde. It is approximately the percentage of this material that nitrifies in about six months.

In summary, it appears from the literature that certain urea-formaldehyde reaction products should prove to be excellent sources of slowly available nitrogen for plant growth. They offer several advantages over the readily soluble sources of nitrogen. Since they release their nitrogen slowly, the leaching of nitrogen is less and nitrogen is provided over a longer period of time. As a result, less frequent applications would be required. These products appear to be better suited to long season crops than to short season crops. However, a mixture of these products with readily soluble sources of nitrogen generally appeared to give a more desirable growth curve.

Urea-formaldehyde products are mixtures of several compounds and the availability of their nitrogen varies with the conditions under which they are produced and the U/F ratios used. Their manufacture therefore requires critical process control in order to produce a suitable product for agronomic use.

The products which seem to offer the most promise are those with U/F ratios ranging from 1.18 to 1.36 and having an availability index of about 49 to 57.

EXPERIMENTAL PROCEDURES

This study was conducted during 1958-60. It was carried out in two phases: a laboratory and a greenhouse phase. The laboratory phase consisted of a study of the nitrification rates of the various materials. The greenhouse phase consisted of pot tests to determine the nitrogen uptake by oats and millet from the various materials.

Description of Soil Used

The soil used throughout this study was a cultivated Lakeland fine sand, a description of which is given in table 1.

Table 1--Description of Lakeland fine sand used in nitrification studies and greenhouse pot tests

Soil	pH	Total N percent	Nitrate N ppm	Pounds per Acre[a]			
				P_2O_5	K_2O	CaO	MgO
Lakeland fine sand	5.6	0.06	4.8	75	132	84	33

[a] Extractable by ammonium acetate solution (pH 4.8).

This soil was selected because of its widespread use in this area for cultivated crops, and also because it is quite typical of the light sandy soils from which soluble fertilizers are readily leached.

Nitrogen Fertilizer Materials Used

Nineteen fertilizer materials[1] were used in this study both for nitrification and greenhouse pot tests. Each material is listed below with analyses, formulations, certain calculated values, and other pertinent information.

1. Nitrogen source 9829
   - By formulation:
     - All nitrogen from inorganic sources
     - 32.0 percent of nitrogen from Nitrana 4M[2]
     - 30.5 percent of nitrogen from ammonium sulfate
     - 37.5 percent of nitrogen from ammonium nitrate
2. Nitrogen source 9830
   - By formulation:
     - 31.7 percent of nitrogen from Nitrana 4M
     - 61.4 percent of nitrogen from urea including urea in N-dure
     - 6.9 percent of nitrogen from ammonium sulfate
     - 214 pounds N-dure per ton of product
   - By analysis:
     - 46.3 percent of nitrogen water-insoluble produced by N-dure and urea
     - 53.7 percent of nitrogen from inorganic sources and urea

---

[1] All fertilizer materials used and the data on their formulations and analyses were supplied by the Nitrogen Division of Allied Chemical Corporation.

[2] A nitrogen fertilizer solution containing 19.0 percent ammonia, 72.5 percent ammonium nitrate, and 8.5 percent water, manufactured by the Nitrogen Division of Allied Chemical Corporation.

3. Nitrogen source 9830-W

    By analysis:

        11.3 percent water-insoluble nitrogen obtained by removing the water-soluble nitrogen from source 9830

4. Nitrogen source 9831

    By formulation:

        31.2 percent of nitrogen from Nitrana 4M

        18.4 percent of nitrogen from ammonium sulfate

        50.4 percent of nitrogen from ureaform[1] (Nitroform[2])

    By analysis:

        60.6 percent of nitrogen water-insoluble from ureaform (Nitroform)

        39.4 percent of nitrogen water-soluble from inorganic sources

5. Nitrogen source 9831-W

    By analysis:

        12.4 percent water-insoluble nitrogen obtained by removing the water-soluble nitrogen from source 9831

6. Nitrogen source 9832

    By formulation:

        61.4 percent of nitrogen from urea including urea in N-dure

        1.0 percent of nitrogen from ammonium sulfate

        25.5 percent of nitrogen from ureaform (Nitroform)

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[1] A general term applied to urea-formaldehyde fertilizer materials.

[2] Trade name of a ureaform material containing 38 percent nitrogen manufactured by Woonsocket Color and Chemical Company.

12.1 percent of nitrogen from aqua ammonia (28 percent ammonia)

214 pounds N-dure per ton of product

By analysis and certain calculated values from formulation:

40.3 percent of nitrogen water-insoluble produced by N-dure and urea

20.1 percent of nitrogen water-insoluble from ureaform

39.6 percent of nitrogen from inorganic sources and urea

7. Nitrogen source 7102

By formulation:

19.7 percent of nitrogen from Nitrana 2M[1]

80.3 percent of nitrogen from urea including urea in N-dure

330 pounds N-dure per ton of product

By analysis:

61.9 percent of nitrogen water-insoluble produced by N-dure and urea

38.1 percent of nitrogen water-soluble from inorganic sources and urea

8. Nitrogen source 7102-W

By analysis:

13.96 percent water-insoluble nitrogen obtained by removing the water-soluble nitrogen from source 7102.

---

[1] A nitrogen fertilizer solution containing 22.2 percent ammonia, 65.0 percent ammonium nitrate, and 12.8 percent water, manufactured by the Nitrogen Division of Allied Chemical Corporation.

9. Nitrogen source 7105

   By formulation:

      11.0 percent of nitrogen from Nitrana 2M

      89.0 percent of nitrogen from urea including urea in N-dure

      307 pounds of N-dure per ton of product

   By analysis:

      62.7 percent of nitrogen water-insoluble produced by N-dure and urea

      37.3 percent of nitrogen water-soluble from inorganic sources and urea

10. Nitrogen source 7105-W

   By analysis:

      13.8 percent water-insoluble nitrogen obtained by removing the water-soluble nitrogen from source 7105.

11. Nitrogen source 7108

   By formulation:

      6.3 percent of nitrogen from ammonia

      93.7 percent of nitrogen from urea including urea in N-dure

      280 pounds N-dure per ton of product

   By analysis:

      18.5 percent of nitrogen water-insoluble produced by N-dure and urea

      81.5 percent of nitrogen water-soluble from inorganic sources and urea

12. Nitrogen source 7108-W

    By analysis:

        8.56 percent water-insoluble nitrogen obtained by removing the water-soluble nitrogen from source 7108.

13. Nitrogen source 9900

    Low solubility ureaform

    By analysis:

        37.51 percent total nitrogen

        35.90 percent water-insoluble nitrogen

        Activity index[1] 58

    Calculated values:

        95.7 percent of nitrogen water-insoluble

        4.3 percent of nitrogen water-soluble

14. Nitrogen source 9537

    Methylenediurea (fertilizer grade)

    By analysis:

        41.3 percent total nitrogen

        10.85 percent water-insoluble nitrogen

        11.17 percent free urea nitrogen

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[1] A method used in evaluating the suitability of urea-formaldehyde materials for fertilizer use based upon differential solubility of the nitrogen in water at 25°C. and in a phosphate-buffered solution of pH 7.5 at 99° to 100°C. The numerical value represents the percentage of the water-insoluble nitrogen, as determined at 25°C., which dissolves in the phosphate-buffered solution.

Calculated values:

26.2 percent of nitrogen water-insoluble

73.8 percent of nitrogen water-soluble

15. Nitrogen source 9538

Methylenediurea (fairly pure)

By analysis:

41.9 percent total nitrogen

0.55 percent water-insoluble nitrogen

1.26 percent free urea nitrogen

Calculated values:

1.3 percent of nitrogen water-insoluble

98.7 percent of nitrogen water-soluble

16. Nitrogen source 9913

Dimethylenetriurea

By analysis:

40.2 percent total nitrogen

8.3 percent water-insoluble nitrogen

Activity index 90

Calculated values:

20.6 percent of nitrogen water-insoluble

79.4 percent of nitrogen water-soluble

17. Nitrogen source 9901

Trimethylenetetraurea

By analysis:

39.38 percent total nitrogen

38.16 percent water-insoluble nitrogen

Activity index 97

Calculated values:

96.9 percent of nitrogen water-insoluble

3.1 percent of nitrogen water-soluble

18. Nitrogen source 9520

Hexamethylenetetramine phosphate

By analysis:

21.9 percent nitrogen (all water-soluble)

27.9 percent phosphorus pentoxide (P_2O_5)

19. Nitrogen source 9539

A highly water-soluble product of unspecified composition

By analysis:

20.9 percent nitrogen

70.8 percent phosphorus pentoxide (P_2O_5)

Description of Fertilizer Materials

Nitrogen sources 9829, 9830, 9831, and 9832 were from 14-7-7 fertilizer formulated as shown in table 2.

Source 9829 contained no water-insoluble nitrogen--the nitrogen being derived from Nitrana 4M, ammonium sulfate, and ammonium nitrate. This source was used in the greenhouse pot tests as a standard representing soluble nitrogen.

In the nitrogen sources containing urea and formaldehyde it will be noted that the formulations and analyses do not always agree. This result is to be expected. The condensation products produced by the reaction of urea with formaldehyde vary with the conditions under which they are produced. Such factors as pH, temperature, reaction time, and others affect the final product. These factors are difficult to control accurately when N-dure is added in fertilizer formulation.

The formulation of source 9830 (table 2) was designed to produce a material having 50 percent of its nitrogen as water-insoluble nitrogen produced by N-dure and 50 percent from soluble sources. By analysis (table 2) this sample contained 13.10 percent total nitrogen and 6.06 percent water-insoluble nitrogen. Therefore, of the total nitrogen in this sample, 46.3 percent was water-insoluble produced by N-dure and 53.7 percent was water-soluble.

Source 9830-W was obtained from 9830 by washing to remove the water-soluble nitrogen according to the procedure outlined by A. O. A. C. [6]. This material contained water-insoluble nitrogen

Table 2--Formulations and product analyses of nitrogen sources 9829, 9830, 9831, and 9832

Research Sample No.	9829	9830	9831	9832
Lot Designation	A	B	C	D
Formulations (lb. material per ton product)				
Normal superphosphate	720	720	720	720
Muriate of potash	240	240	240	240
Nitrana 4M (19.0% NH_3, 72.5% NH_4NO_3) 41% N	221	221	221	0
N-dure (59% HCHO, 26% urea) 12.1% N	0	214	0	214
Urea (46.5% N)	0	322	0	322
Ammonium sulfate (20.5% N)	421	96	260	14
Ammonium nitrate (33.5% N)	318	0	0	0
Pearlite (filler)	0	211	95	263
Dolomite	100	100	100	100
Ureaform (Nitroform) 38% N	0	0	384	192
Aqua ammonia (28% NH_3) 23.0% N	0	0	0	150
Product Analysis (weight percent)				
Total nitrogen	14.35	13.10	14.26	14.33
Water insoluble N	0	6.06	5.62	8.65
Activity index	---	38.9	53.7	43.2
Soluble ureaform	0	1.18	1.46	2.66
Free urea N	0	1.58	0.62	1.44
Ammonia N	---	3.06	4.70	1.88
Nitrate N	---	1.22	1.86	0
Total P_2O_5	7.76	7.58	7.48	7.49
Citrate insoluble P_2O_5	0.23	0.43	0.26	0.33
K_2O	7.12	7.19	6.84	7.16
Water	1.69	6.09	3.64	5.00
Calculated Values				
Total lbs. of N per ton (by formulation)	283	286	290	286
% Water-insoluble N of total N[a]	0	46.3	39.4	60.4
% Water soluble N of total N[a]	100	53.7	60.6	39.6
% Nitrate N of total N	28.4	10.7	9.9	0
Urea/formaldehyde mole ratio	0	0.67	---	0.67

[a] Calculated from product analysis.

produced only by N-dure, thereby making it possible to study the characteristics of this form of nitrogen directly without water-soluble sources being present. This sample contained 11.3 percent nitrogen.

The formulation of source 9831 (table 2) was designed to produce a material having 50 percent of its nitrogen as water-insoluble nitrogen from ureaform (Nitroform) and 50 percent from soluble sources. By analysis (table 2) this source contained 14.26 percent total nitrogen and 5.62 percent water-insoluble nitrogen. Accordingly, of the total nitrogen, 39.4 percent was water-insoluble derived from ureaform (Nitroform) and 60.6 percent was water-soluble.

Source 9831-W was derived from 9831 in the same manner as that described above for 9830-W. However, 9831-W contained water-insoluble nitrogen from ureaform (Nitroform). It was therefore similar to 9830-W in that the only important difference in the two materials was the source of the water-insoluble nitrogen.

The formulation used in the preparation of source 9832 (table 2) was designed to produce a material having 50 percent of its nitrogen as water-insoluble produced by N-dure, 25 percent as water-insoluble derived from ureaform (Nitroform), and 25 percent derived from soluble sources. However, the analysis shows that the product did not conform to the exact percentages intended by formulation. By analysis, this material (9832) contained 14.33 percent total nitrogen and 8.65 percent water-insoluble nitrogen. Accordingly, of the total nitrogen it contained, 60.4 percent was water-insoluble and 39.6 percent was water-soluble.

Of the 60.4 percent water-insoluble nitrogen, 20.1 percent is attributed to ureaform (Nitroform) and 40.3 percent to that produced by N-dure. These two forms of water-insoluble nitrogen are not distinguishable by analysis, but the above percentages correspond to the formulation. Therefore the material contained 20.1 percent of its nitrogen as water-insoluble nitrogen derived from ureaform (Nitroform), 40.3 percent as water-insoluble nitrogen produced by N-dure, and 39.6 percent from soluble sources.

Sources 7102, 7105, and 7108 were also 14-7-7 fertilizers and were formulated as shown in table 3. The formulation was designed to produce products of low, medium, and high nitrogen solubility by using varying amounts of N-dure in the formulation. The product analysis showed that the percentage of water-insoluble nitrogen of the total nitrogen in sources 7102, 7105, and 7108 was 61.9 percent, 62.7 percent, and 18.5 percent respectively. It will be noted that 7102 and 7105 contained about the same percent of water-insoluble nitrogen; however, this does not necessarily mean that the nitrogen availability would be the same.

Sources 7102-W, 7105-W, and 7108-W were obtained by removing the water-soluble nitrogen from sources 7102, 7105, and 7108 respectively, as described previously for 9830-W and 9831-W. These sources, therefore, contained the water-insoluble nitrogen produced by the use of N-dure.

Table 3--Formulations and product analyses of nitrogen sources 7102, 7105, and 7108

Research Sample No. Nitrogen Solubility	7102 Low	7105 Medium	7108 High
Formulations (lb. material per ton product)			
Superphosphate (19.7% APA)	561	646	726
Triple superphosphate (46.1% APA)	71	34	0
Muriate of potash (59.4% K_2O)	241	241	241
Nitrana 2M (22.2% NH_3, 65% NH_4NO_3) 41% N	137	77	0
Anhydrous ammonia (82.5% N)	0	0	22
N-dure (59% HCHO, 26% urea) 12.1% N	330	307	280
Urea (46.5% N)	406	470	511
Vermiculite	300	250	250
Dolomite	100	100	77
Product Analysis (weight percent)			
Total N	14.37	14.08	15.00
Water-insoluble N	8.90	8.83	2.77
Hot water-insoluble N	7.64	5.01	0.80
Activity index	15	43	71
Free urea N	0.97	2.22	4.77
Total P_2O_5	7.33	7.31	7.45
K_2O	7.16	7.90	7.57
Water	1.7	2.9	0.77
Calculated Values			
Total pounds N per ton (by formulation)	285	287	290
Urea/formaldehyde mole ratio	1.25	1.50	1.75
Water-soluble ureaform N	1.33	1.55	5.86
Percent of total N as ureaform N	71.3	73.7	57.5
Percent of total urea N charged as ureaform N	91.5	82.4	64.3
Percent of ureaform N as water-soluble N	13.0	14.9	67.9
Percent of ureaform N as water-insoluble N	87.0	85.1	32.1
Percent nitrate N	0.78	0.44	0
Percent nitrate N of total N	5.4	3.1	0
Percent water-insoluble N of total N[a]	61.9	62.7	18.5
Percent water-soluble N of total N[a]	38.1	37.3	81.5

[a] Calculated from product analysis.

Source 9520 was hexamethylenetetramine phosphate and is a possible reaction product when N-dure is used in the ammoniation of superphosphate. Therefore, it was included in this study.

Sources 9537, 9538, 9901, and 9913 were all forms of methylene ureas. These are materials which are believed to be intermediate products formed when urea and formaldehyde react and resinify.

The exact composition of source 9539 was not specified by the supplier (Nitrogen Division of Allied Chemical Corporation) except that it was highly water soluble and contained 20.9 percent nitrogen and 70.8 percent P_2O_5.

Source 9900 was a laboratory sample of low solubility ureaform containing 37.5 percent total nitrogen and 35.9 percent water-insoluble nitrogen.

Laboratory Nitrification Studies

These studies were conducted in three series of tests carried out at different times but each following in close sequence.

Each series of tests was conducted by mixing 100 parts per million of nitrogen from the various sources with limed and unlimed soil in one quart incubation jars aerated by means of a 5 mm. hole through the lid. The amount of soil used in each jar was 500 grams. This was sufficient to permit the repeated removal of samples for nitrate nitrogen analysis over the period of study. The jars were kept in an incubator where the temperature was held constant at 28°C. Soil moisture was maintained at 50 to 75 percent of field capacity by weighing the jars and contents periodically and replenishing the water as needed. A 50 gram sample of soil was removed from each jar at the end of 1, 2, 4, 8, and 12 weeks and analyzed for nitrate nitrogen by the phenoldisulfonic acid method as described by Harper [26]. A Cenco type B2 colorimeter was used.

The nitrogen sources used in series 1 are shown in table 4. All treatments were carried out in duplicate except the urea treatment, check, and check plus lime which were conducted in triplicate. Urea was included in all three series of tests as a standard representing a soluble source of nitrogen. The checks were conducted in triplicate in all three series of tests in order to get a better measure of the nitrification taking place in the soil in which no nitrogenous fertilizer materials were added. The amount of nitrate produced in the check soil was particularly important since it was necessary to deduct it from the values obtained for soils to which the nitrogenous materials were added for nitrification.

The nitrogen sources used in series 2 are shown in table 5. It will be noted that nitrogen source 9520 was repeated in this series. The repetition was carried out in order to substantiate the low nitrification obtained under unlimed soil conditions in series 1 for this material.

The nitrogen sources used in series 3 are shown in table 6. Calcium nitrate was included in this series of tests to determine whether or not denitrification was occurring to any appreciable extent.

Table 4--Treatments for laboratory nitrification studies.
Series 1.

Treatment No.	N Source	Rate of N ppm	No. of Reps.
1	9829	100	2
2	9829 + lime	100	2
3	9830	100	2
4	9830 + lime	100	2
5	9830-W	100	2
6	9830-W + lime	100	2
7	9831	100	2
8	9831 + lime	100	2
9	9831-W	100	2
10	9831-W + lime	100	2
11	9832	100	2
12	9832 + lime	100	2
13	9520	100	2
14	9520 + lime	100	2
15	9537	100	2
16	9537 + lime	100	2
17	9538	100	2
18	9538 + lime	100	2
19	9539	100	2
20	9539 + lime	100	2
21	Urea	100	3
22	Urea + lime	100	3
23	Check	0	3
24	Check + lime	0	3

Note:

Lime was applied in the form of reagent grade calcium carbonate at the rate of 5,000 pounds per 2,000,000 pounds of soil.

Table 5--Treatments for laboratory nitrification studies.
Series 2.

Treatment No.	N Source	Rate of N ppm	No. of Reps.
1	9520	100	2
2	9520 + lime	100	2
3	9900	100	2
4	9900 + lime	100	2
5	9901	100	2
6	9901 + lime	100	2
7	9913	100	2
8	9913 + lime	100	2
9	Urea	100	2
10	Urea + lime	100	2
11	Check	0	3
12	Check + lime	0	3

Note:

Lime was applied in the form of reagent grade calcium carbonate at the rate of 5,000 pounds per 2,000,000 pounds of soil.

Table 6--Treatments for laboratory nitrification studies.
Series 3.

Treatment No.	N Source	Rate of N ppm	No. of Reps.
1	7102	100	2
2	7102 + lime	100	2
3	7102-W	100	2
4	7102-W + lime	100	2
5	7105	100	2
6	7105 + lime	100	2
7	7105-W	100	2
8	7105-W + lime	100	2
9	7108	100	2
10	7108 + lime	100	2
11	7108-W	100	2
12	7108-W + lime	100	2
13	$Ca(NO_3)_2$	100	3
14	$Ca(NO_3)_2$ + lime	100	3
15	Urea	100	2
16	Urea + lime	100	2
17	Check	0	3
18	Check + lime	0	3

Note:

Lime was applied in the form of reagent grade calcium carbonate at the rate of 5,000 pounds per 2,000,000 pounds of soil.

Greenhouse Pot Tests

These tests were conducted in two series in two-gallon glazed earthenware pots. The first series was carried out during the period December 29, 1958, to June 26, 1959; the second series, during the period December 18, 1959 to April 21, 1960. Each series consisted of primary treatment and growth of oats, followed by growth of millet without further addition of nitrogen fertilizer. In each series the oats were clipped twice, dried, weighed, and analyzed for total nitrogen; the oat roots were removed, washed, dried, weighed, and analyzed for total nitrogen; and the millet was clipped, dried, weighed, and analyzed for total nitrogen. All nitrogen determinations were made by the Kjeldahl method [6] using copper as the digestion catalyst and distilling ammonia into a 0.67 percent boric acid solution. Semimicro apparatus was used for both the digestion and distillation.

In each series the soil was brought into the greenhouse and allowed to dry slightly. It was then passed through a one-fourth inch screen to remove any particles of undecomposed plant materials which may have been present. A glass wool plug was placed in the hole in the bottom of each pot and about one quart of gravel added. This was done in order to provide aeration in the bottom of the pot. The method of watering did not make drainage necessary. There was a total of 72 pots in the first series and 91 in the second series. Twenty pounds of soil were weighed out and placed in each of the two-gallon pots. The nitrogenous fertilizer materials together with enough superphosphate (20 percent P_2O_5) and muriate of potash (60 percent K_2O) to give 200 pounds of

P_2O_5 and 200 pounds of K_2O per acre were then mixed with the top 6 inches of soil in each pot. The fertilizer materials were added on surface area basis of 0.37 square feet per pot. There were three replicates of each treatment and six replicates of the check. A completely randomized design was used.

In series 1 (table 7) three rates of nitrogen were used without lime. This series was more or less exploratory and designed primarily to determine what might be expected from the various materials in the way of nitrogen recovery, and the proper nitrogen rate to use so that the second series could be more intelligently planned. Thirty-five seeds of Seminole oats were planted in each pot. As soon as the seedlings were established they were thinned to 25 plants per pot. Moisture was controlled by addition of deionized water in the morning when a pot showed a dry soil surface. The amount added was sufficient to carry the pot over one morning without watering but to show a dry surface the second morning. This prevented waterlogging but kept the pots as close to field capacity as practical. Subsequent observation of the development of roots in the pots verified that proper moisture control had been practiced. The oats were clipped 56 days after planting and again 38 days later. Each clipping was dried at 70°C., weighed, and analyzed for nitrogen. The oat roots were removed, washed, dried, weighed, and analyzed for nitrogen.

Ten Cattail millet seed were then planted in each pot and the plants later thinned to five per pot. The millet was clipped 26 days

Table 7--Fertilizer treatments applied in greenhouse pot tests.
Series 1.

Treatment No.	N Source	Rate in Lb./Acre N	P_2O_5	K_2O	No. of Reps.
1	9829	50	200	200	3
2	9829	100	200	200	3
3	9829	200	200	200	3
4	9830	50	200	200	3
5	9830	100	200	200	3
6	9830	200	200	200	3
7	9830-W	50	200	200	3
8	9830-W	100	200	200	3
9	9830-W	200	200	200	3
10	9831	50	200	200	3
11	9831	100	200	200	3
12	9831	200	200	200	3
13	9831-W	50	200	200	3
14	9831-W	100	200	200	3
15	9831-W	200	200	200	3
16	9832	50	200	200	3
17	9832	100	200	200	3
18	9832	200	200	200	3
19	9520	100	200	200	3
20	9537	100	200	200	3
21	9538	100	200	200	3
22	9539	100	200	200	3
23	Check	0	200	200	6

Table 8--Fertilizer treatments applied in greenhouse pot tests. Series 2.

Treatment No.	N Source	Rate in pounds per acre N	P_2O_5	K_2O	Es-Min-El[a]	No. of Reps.
1	9829	100	200	200	100	3
2	9829 + lime	100	200	200	100	3
3	9830	100	200	200	100	3
4	9830 + lime	100	200	200	100	3
5	9830-W	100	200	200	100	3
6	9830-W + lime	100	200	200	100	3
7	9831	100	200	200	100	3
8	9831 + lime	100	200	200	100	3
9	9831-W	100	200	200	100	3
10	9831-W + lime	100	200	200	100	3
11	9832	100	200	200	100	3
12	9832 + lime	100	200	200	100	3
13	9520	100	200	200	100	3
14	9520 + lime	100	200	200	100	3
15	9538	100	200	200	100	3
16	9538 + lime	100	200	200	100	3
17	7102 + lime	100	200	200	100	3
18	7102-W + lime	100	200	200	100	3
19	7105 + lime	100	200	200	100	3
20	7105-W + lime	100	200	200	100	3
21	7108 + lime	100	200	200	100	3
22	7108-W + lime	100	200	200	100	3
23	9900 + lime	100	200	200	100	3
24	9901 + lime	100	200	200	100	3
25	9913 + lime	100	200	200	100	3
26	9830-W	1000	200	200	100	2
27	9830-W + lime	1000	200	200	100	2
28	Check	0	200	200	100	6
29	Check + lime	0	200	200	100	6

[a] Es-Min-El is a trace element mixture containing boron, zinc, copper, manganese, and iron and is manufactured by Tennessee Corporation.

Note:

All lime was applied in the form of dolomite at the rate of 2,000 pounds per 2,000,000 pounds of soil.

after planting and again 36 days later. The two clippings were composited, dried, weighed, and analyzed for nitrogen.

In series 2, the preparation of the soil, application of the fertilizer materials, planting and clipping of oats, removal of oat roots, planting and clipping of millet, and analysis of oats, oat roots, and millet were carried out in a manner similar to that in series 1. All nitrogen sources were applied at the rate of 100 pounds of nitrogen per acre (table 8). One material, 9830-W was applied also at 1,000 pounds of nitrogen per acre as a supplementary exploratory test. Most of the fertilizer materials were applied to both limed and unlimed soil although certain tests which had appeared in series 1 without lime were omitted. Es-Min-El was used throughout this series to avoid possible trace element deficiencies. Surgrain variety of oats was used instead of Seminole. Just prior to planting the millet, additional phosphorus and potassium were added to each pot in solution form from $CaH_4(PO_4)_2 \cdot H_2O$ and K_3PO_4 to give 100 pounds each of P_2O_5 and K_2O per acre.

Statistical Methods

The data were analyzed by the analysis of variance methods described by Snedecor [43]. Comparisons among means were based on the multiple range test [19].

RESULTS AND DISCUSSION

Data from the studies on the rates of nitrification of various nitrogen sources are presented graphically in the form of curves. It will be noted that the curves do not start at the zero point on the graph. The point at which they start represents the initial nitrate nitrogen present in the soil. Some of the fertilizer materials contained nitrate nitrogen and in such cases the point at which the curve starts represents the nitrate nitrogen in the soil plus what was present in the fertilizer material. The nitrate nitrogen produced in the untreated soil was deducted from the values found for the various materials. The nitrification curves for the untreated soil in the three series of tests are shown in figures 1, 2, and 3.

The summarized data on nitrogen uptake from the various materials by oats and millet in the greenhouse pot tests are presented in tabular form. The values for the percent of applied nitrogen recovered represent the percent total nitrogen recovered minus the recovery by the appropriate check.

Each fertilizer material will be discussed individually. Its nitrification in the laboratory, effects on yield of oats, oat roots, and millet, and nitrogen uptake from the greenhouse pot tests will be considered collectively. Since the first greenhouse series was somewhat of an exploratory nature, the nitrogen uptake from the various materials used in the greenhouse pot tests will be discussed primarily from the standpoint of the second series.

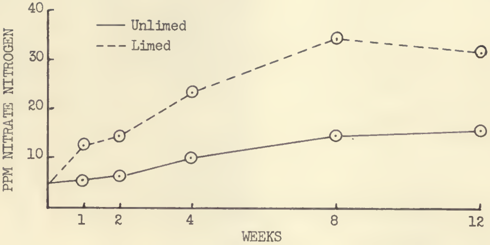

Figure 1--Nitrification in untreated soil. Series 1.

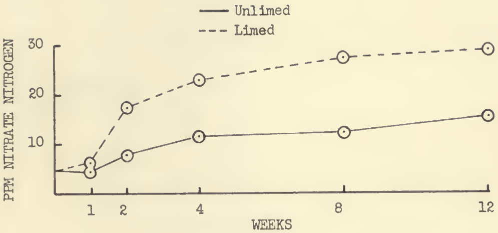

Figure 2--Nitrification in untreated soil. Series 2.

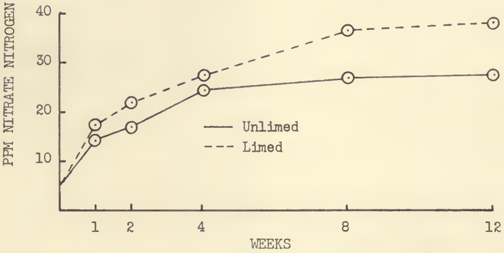

Figure 3--Nitrification in untreated soil. Series 3.

Nitrogen source 9829

This source contained only water-soluble nitrogen. It will be noted in table 9 that the total nitrogen recovery was quite high. However, in the unlimed soil more than one-half of the net total nitrogen absorbed by the crops was absorbed by the oats in the first 42 days, and more than 90 percent in the first 73 days, whereas the millet recovery was less than 2 percent of the net total absorbed. The oat roots recovered twice as much nitrogen from the limed soil as from the unlimed soil but there was no net recovery of nitrogen by the millet during 48 days of growth in the limed soil. The millet suffered extreme nitrogen deficiency because of the previous high nitrogen recovery by the oats.

The total nitrogen recovery was about 4 percent higher from the limed soil than from the unlimed soil but this difference was not statistically significant.[1] However, this result is supported by the nitrification curve shown in figure 4 in which nitrification of this material was greater under limed conditions. Apparently some denitrification or calculated nitrogen deficit occurred during the first week, but this was reversed after that time and nitrates increased thereafter except at the eighth week. A certain amount of denitrification is to be expected according to the results obtained with calcium nitrate (figure 5). The temporary depression of nitrification observed at eight

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[1] Any statement concerning statistical significance is based on analysis of variance and multiple range tests shown in tables 14 through 29 in Appendix.

Table 9--Nitrogen recovery by oats and millet from various sources when applied at the rate of 100 pounds of nitrogen per acre (except as noted) to Lakeland fine sand in greenhouse pot tests. Series 2.

N Source	Percent of Applied Nitrogen Recovered[a] 1st oat clipping (42 days)	2nd oat clipping (31 days)	Oat roots	Millet (48 days)	Total
9829	38.3	26.1	5.1	1.2	70.9
9829 + lime	40.0	24.8	10.3	0.0	75.1
9830	28.5	6.7	5.4	2.8	43.4
9830 + lime	28.5	7.9	7.2	0.8	44.4
9830-W	9.5	3.9	4.3	3.9	21.6
9830-W + lime	7.0	2.8	7.0	3.2	20.0
9831	29.6	6.4	4.4	2.0	42.4
9831 + lime	29.4	9.2	5.8	1.1	45.5
9831-W	4.5	1.1	0.9	1.4	7.9
9831-W + lime	2.7	0.3	2.5	0.4	5.9
9832	22.9	6.9	7.4	1.9	39.1
9832 + lime	20.4	8.4	11.8	1.0	41.6
9520	54.1	17.8	10.4	1.1	83.4
9520 + lime	49.3	21.1	6.6	1.1	78.1
9538	49.5	19.4	8.0	1.0	77.9
9538 + lime	48.1	20.6	8.7	0.4	77.8
7102 + lime	19.9	7.0	6.6	0.4	33.9
7102-W + lime	7.4	3.4	5.9	3.0	19.7
7105 + lime	26.2	10.2	8.2	1.1	45.7
7105-W + lime	8.4	6.7	9.7	3.3	28.1
7108 + lime	41.5	18.2	8.0	1.3	69.0
7108-W + lime	18.5	7.9	7.8	3.2	37.4
9900 + lime	27.4	10.4	6.8	2.3	46.9
9901 + lime	39.6	15.7	15.6	1.3	72.2
9913 + lime	49.6	16.1	8.9	0.7	75.3
9830-W[b]	9.0	10.0	2.0	4.9	25.9
9830-W[b] + lime	8.3	9.1	1.7	3.5	22.6

[a] Average of three replicates.

[b] 1,000 pounds nitrogen per acre; two replicates.

Notes:

All lime applied in the form of dolomite at the rate of 2,000 pounds per 2,000,000 pounds of soil.

The number of days stated refers to actual growth period of the clipping.

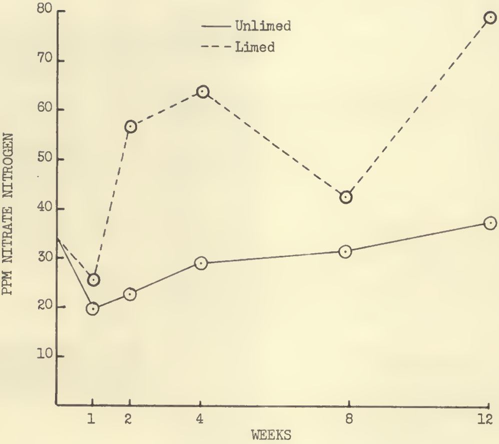

Figure 4--Nitrification of source 9829. Series 1.

All of nitrogen from inorganic sources.

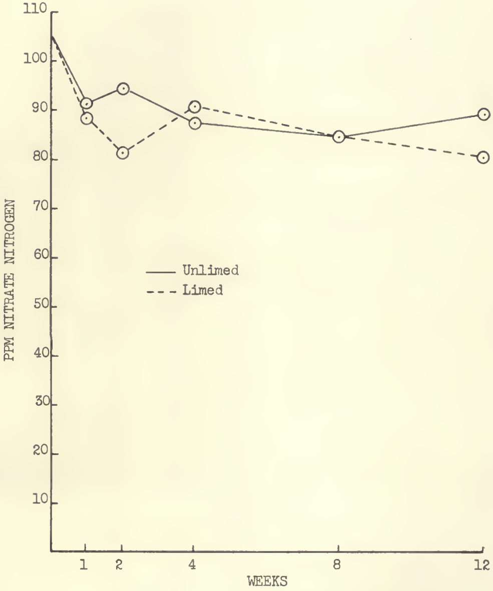

Figure 5--Recovery of nitrate nitrogen from calcium nitrate. Series 3.

weeks with most limed tests is quite typical of secondary effects of microbiological population shifts during a study of this type.

It is apparent from the above results that this fertilizer material has poor distribution of available nitrogen over the growth period of oats and millet. The nitrogen became available immediately and was therefore taken up by the oats leaving very little for the millet. This is typical of readily soluble sources of nitrogen.

Nitrogen source 9830

This source contained 46.3 percent of its total nitrogen as water-insoluble nitrogen which was N-dure produced. As would be expected the net total nitrogen recovery as shown in table 9 was considably less than from source 9829. However, approximately 65 percent of the total nitrogen absorbed by the two crops was recovered in the first 42 days in both the limed and unlimed soil but only 15 to 18 percent in the following 31 days for a total of about 80 percent for the oats. Even though 46 percent of the nitrogen in this material was water-insoluble, the results clearly show that much of the nitrogen became available during the early stages of growth. There was slightly more nitrogen recovery from this material by millet than from source 9829 which reflects the slightly longer lasting effects of the water-insoluble nitrogen. This recovery, however, was very low.

The nitrification curve (figure 6) for this material shows that less nitrates were produced over the 12 weeks period than were produced from source 9829, which might be expected since this material (9830) contained water-insoluble nitrogen. Nitrate production was higher under limed conditions than unlimed conditions.

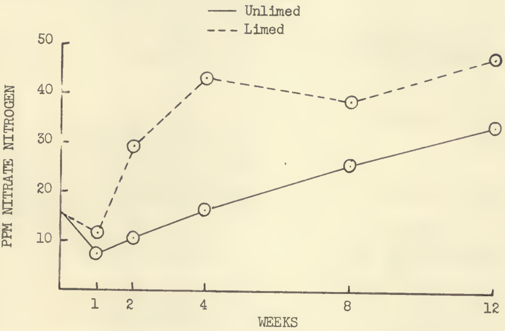

Figure 6--Nitrification of source 9830. Series 1.

46.3 percent of nitrogen water-insoluble from N-dure.

Nitrogen source 9830-W

This source contained only water-insoluble nitrogen produced by N-dure. It will be noted in table 8 that this material was used at the rate of 1,000 pounds of nitrogen per acre as well as at the 100 pound rate.

At the 100 pound rate it will be noted that the nitrogen uptake distribution was quite favorable except for the first clipping of oats in which appeared approximately 44 percent and 35 percent of the net total nitrogen recovered from the unlimed and limed soils respectively. The millet recovered essentially the same percentage of nitrogen as the second clipping of oats; however, the millet grew for 48 days as compared to 31 days for the oats. This is important because it clearly shows that the nitrogen became available over a longer period of time than did the nitrogen from soluble sources. In table 10 it will be noted that the yield of the first and second clippings of oats was approximately 20 percent less than the yield from the soluble source of nitrogen (9829), but the millet yield was greater from this source (9830-W) than from the soluble source. Data presented in tables 9 and 10 indicate that approximately one-fourth of the net nitrogen absorbed by the crops appeared in the first clipping of oats and gave yields comparable to those from soluble sources. The 9.5 percent and 7.0 percent recovery of nitrogen applied in this form by the first clipping of oats was very low. It is important to note that the percent nitrogen recovery (table 9) by oats and millet was less from limed soil than from unlimed soil. However, the reverse was true with oat roots.

Table 10--Yield of oats and millet from various sources when applied at the rate of 100 pounds of nitrogen per acre (except as noted) to Lakeland fine sand in greenhouse pot tests. Series 2.

	Yield in Grams per Pot (Average of 3 Replicates)				
N Source	1st oat clipping (42 days)	2nd oat clipping (31 days)	Oat roots	Millet (48 days)	Total
9829	4.9	5.0	6.5	2.2	18.6
9829 + lime	5.0	4.9	7.7	2.2	19.8
9830	4.9	3.5	8.1	2.9	19.4
9830 + lime	4.6	3.3	7.7	2.9	18.5
9830-W	3.9	2.7	7.4	3.3	17.3
9830-W + lime	3.7	2.5	9.0	4.2	19.4
9831	5.0	3.4	8.4	2.6	19.4
9831 + lime	4.5	3.5	8.2	2.8	19.0
9831-W	3.6	2.3	6.7	2.2	14.8
9831-W + lime	3.4	2.3	7.9	2.6	16.2
9832	4.9	3.4	9.1	1.2	19.7
9832 + lime	4.7	3.5	11.1	3.0	22.3
9520	6.3	4.0	10.6	2.3	23.2
9520 + lime	5.7	4.6	7.2	2.9	20.4
9538	5.8	4.2	8.5	2.1	20.6
9538 + lime	5.7	4.6	8.9	2.9	22.1
7102 + lime	4.3	3.2	7.4	2.7	17.6
7102-W + lime	4.0	3.0	8.7	3.8	19.5
7105 + lime	4.7	3.8	8.1	3.0	19.6
7105-W + lime	3.7	3.3	9.5	3.9	20.4
7108 + lime	5.2	4.5	8.1	3.2	21.0
7108-W + lime	4.3	3.4	8.5	4.1	20.3
9900 + lime	4.8	3.5	8.1	3.5	19.9
9901 + lime	6.0	4.5	10.5	3.2	24.2
9913 + lime	6.1	4.4	8.1	3.1	21.7
9830-W[a]	7.8	9.5	8.2	15.9	41.4
9830-W[a] + lime	7.7	7.9	6.3	15.3	37.2
Check[b]	3.3	2.2	7.2	1.7	14.4
Check + lime[b]	3.5	2.3	6.1	2.5	14.4

[a] 1,000 pounds nitrogen per acre; two replicates.

[b] Average of 6 replicates.

Notes:

All lime was applied in the form of dolomite at the rate of 2,000 pounds per 2,000,000 pounds of soil.

The number of days stated refers to actual growth period of the clipping.

Higher total net nitrogen in the roots under unlimed soil conditions is supported by the data presented in figure 7 which clearly shows greater nitrate production under these conditions. This is in agreement with the results obtained by Winsor and Long [48].

The 1,000 pound rate of nitrogen gave a more favorable nitrogen uptake distribution for plant growth than did the 100 pound rate. The first two clippings of oats recovered approximately the same percentage of the applied nitrogen. The nitrogen recovery by the millet was lower, but was still quite high compared to other nitrogen sources. The total percentage of applied nitrogen recovered was not greatly different from that recovered at the 100 pound rate but the net total quantity of nitrogen recovered was about ten times greater. The percentage of nitrogen recovered by the oat roots approximated that from 9831-W, and recovery from both 9830-W and 9831-W were considerably lower than from any other source.

It is important to note in table 10 that the yield of oats and millet with 9830-W at 1,000 pounds of nitrogen per acre was greater than from the soluble source (9829). Although the total amount of nitrogen taken up by the first oat clipping from 9829 was greater than from 9830, there was no increase in yield. In the case of 9830-W, at the 1,000 pound of nitrogen per acre rate, the total amount of nitrogen taken up by the first clipping was greater than from 9829 and was accompanied by a considerable increase in yield. This point is significant in that it indicates that controlled nitrogen supply will give greater gross yield.

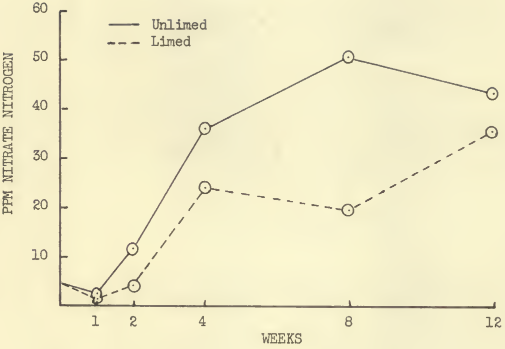

Figure 7--Nitrification of source 9830-W. Series 1.

All nitrogen water-insoluble from N-dure.

The yield of the second clipping of oats from the unlimed soil containing 9830-W at the 1,000 pound rate of nitrogen per acre was approximately 90 percent greater than from the soluble source of nitrogen (9829) at 100 pounds per acre.

The millet yield was approximately 620 percent greater from source 9830-W at 1,000 pounds of nitrogen per acre than from the soluble source (9829), but this fact is not as significant as it might appear since nitrogen was very limiting in the growth of the millet from the latter source which was applied at the rate of 100 pounds of nitrogen per acre. The total yield was more than 100 percent greater than from the soluble source even though nitrogen appeared to be limiting only to the millet and not to the oats in the case of the soluble source.

Nitrogen source 9831

This fertilizer material was similar to 9830 but contained water-insoluble nitrogen derived from ureaform (Nitroform) rather than from N-dure. The percent of water-insoluble nitrogen, based on the total nitrogen in this material, was 39.4 percent as compared to 46.3 percent for 9830. The similarity of the two materials with respect to nitrate production is shown in figures 6 and 8. The two curves are almost identical. Nitrate production (figure 8) was much greater during the first 8 weeks under limed conditions than under unlimed conditions indicating that the easily nitrifiable materials (ammonium sulfate and ammonium nitrate) contained in this sample dominated nitrate production during this period. Urea (figure 9), ammonium sulfate, and

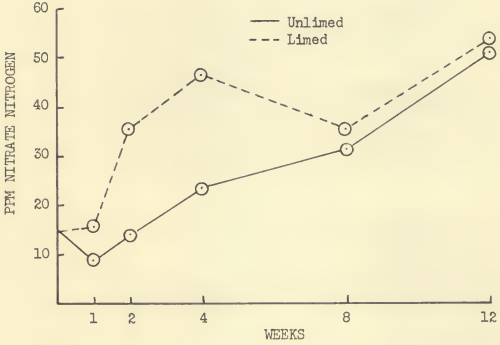

Figure 8--Nitrification of source 9831. Series 1.

39.4 percent of nitrogen water-insoluble from ureaform (Nitroform).

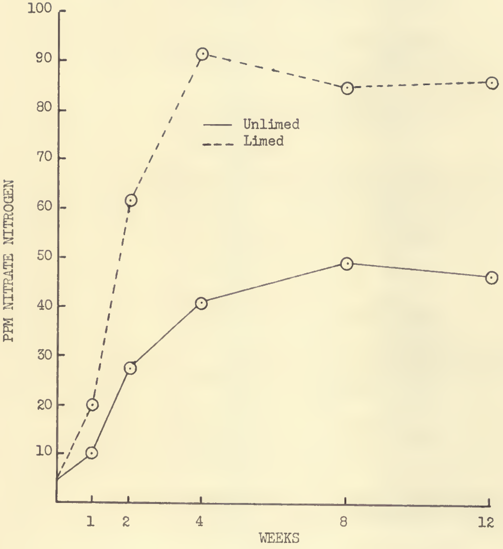

Figure 9--Nitrification of urea. Series 1.

ammonium nitrate nitrify more rapidly under limed conditions, but ureaform materials (figure 7) nitrify more rapidly under more acid conditions; hence in mixtures the two effects tend to even out the curve.

The similarity of the two materials (9830 and 9831) is again noted in table 9 where the percentage of applied nitrogen recovered was practically the same from oats and millet. The yields (table 10) were also almost identical. Although the total nitrogen in 9831 was 7 percent more water-soluble than in source 9830, the difference was not reflected in the results obtained.

The data for this material (9831) indicated that there was little if any difference between the availability of the nitrogen produced by N-dure and the nitrogen in ureaform (Nitroform). Any difference that existed was either too small to measure, was cancelled out because of the difference in percentage of water-soluble nitrogen present, or was masked by the other variation in the sources of nitrogen used in the formulation (table 2).

Nitrogen source 9831

This material contained water-insoluble nitrogen from ureaform (Nitroform) only. It was practically identical to 9830-W except that the water-insoluble nitrogen in 9830-W was derived from N-dure. A comparison of the results obtained with these two materials is in effect, a comparison of the water-insoluble nitrogen in ureaform (Nitroform) and the water-insoluble nitrogen produced by N-dure.

There was very little difference in the yield (table 10) of oats from 9830-W and 9831-W under either limed or unlimed conditions. However, the millet yield was 50 to 60 percent greater from 9830-W than from 9831-W under the same conditions. In comparing unlimed with limed conditions, it is noted (table 9) that in every case, except oat roots, nitrogen recovery was less under limed conditions. This result is supported by the data presented in figure 10 which shows that nitrate production was less under limed soil conditions. Table 9 shows that the percent of applied nitrogen recovered from 9831-W by the first clipping of oats was approximately one-half that from 9830-W and the recovery from 9831-W + lime was approximately one-third that from 9830-W + lime. These differences were as great or greater for the second clipping of oats, oat roots, and millet. Under unlimed conditions the total percent of applied nitrogen recovered from 9830-W was approximately 2.7 times greater than that from 9831-W and approximately 3.4 times greater under limed soil conditions.

From the above results it is apparent that the water-insoluble nitrogen in ureaform (Nitroform) is more slowly available than the water-insoluble nitrogen produced by N-dure.

Nitrogen source 9832

This product contained 39.6 percent of the total nitrogen as water-soluble nitrogen and 60.4 percent as water-insoluble nitrogen in which 40.3 percent was attributed to that produced by N-dure and the remaining 20.1 percent attributed to ureaform (Nitroform) by the formulation.

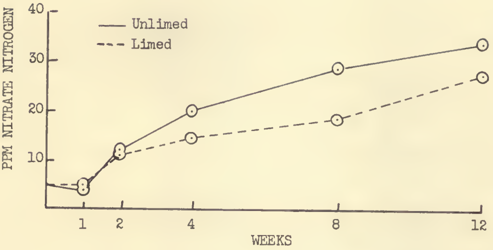

Figure 10--Nitrification of source 9831-W. Series 1.

All nitrogen water-insoluble from ureaform (Nitroform).

According to the amount of water-soluble nitrogen contained in this material (9832), the nitrogen uptake by the first clipping of oats should be less than from either 9830 or 9831. Table 9 bears out this point.

Under unlimed soil conditions, the percent of applied nitrogen recovered was approximately three times higher in the first clipping of oats than in the second, which in turn was about three times higher than that recovered by the millet. A similar relationship existed in the limed soil but the difference between the second clipping of oats and the millet was even more extreme. From these results it appears that the distribution of nitrogen uptake from this mixture leaves much to be desired.

A comparison of the percent of applied nitrogen recovered under unlimed soil conditions versus limed conditions (table 9) reveals that there is practically no difference between the two. The result is supported by the nitrate production curve for this material shown in figure 11. Although nitrate production was greater in the limed soil during the first seven weeks, the reverse was true thereafter.

Total yields from material 9832 (table 10) were essentially the same as yields from 9829, 9830, and 9831. It is interesting to note that even though there was approximately 39 percent nitrogen recovery by the first clipping of oats from 9829 and approximately 21 percent recovery from 9832, the yield was practically the same. It appears that about 20 percent recovery by the first clipping of oats furnishes sufficient nitrogen to give maximum yield.

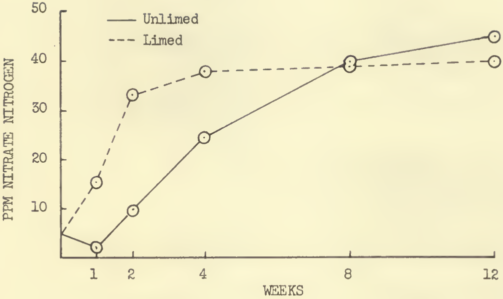

Figure 11--Nitrification of source 9832. Series 1.

20.1 percent of nitrogen water-insoluble from ureaform (Nitroform).

40.3 percent of nitrogen water-insoluble from N-dure.

The nitrogen uptake distribution shows that about one-half of the nitrogen recovered from 9832 was in the first oat clipping even though the nitrogen was more slowly available than from a soluble source and yields practically the same.

Nitrogen source 9520

This source was the compound, hexamethylenetetramine phosphate. It contained 21.9 percent nitrogen and is believed to be formed when N-dure is used in the ammoniation of superphosphate.

The ease with which the nitrogen in this compound becomes available is evident from the data in table 9. Approximately 50 percent of the applied nitrogen was recovered by the first clipping of oats as compared to about 40 percent from 9829 which contained such soluble sources of nitrogen as ammonium nitrate and ammonium sulfate. The second clipping of oats recovered about 5 to 9 percent less of the applied nitrogen from 9520 than from 9829, but the total nitrogen recovery was approximately 5 percent greater from 9520 than from 9829.

The nitrogen uptake distribution from 9520 was less favorable than from 9829. Of the net total nitrogen absorbed, about 65 percent was recovered by the first clipping of oats from 9520 as compared to about 54 percent from 9829. These recoveries were somewhat reversed in the second clipping of oats where approximately 25 percent of the absorbed nitrogen was recovered from 9520 as compared to 35 percent for 9829.

According to the nitrate production curves (figures 12 and 13) for 9520 it would appear that nitrogen recovery should have been much higher under limed soil conditions than from unlimed, but such was not the case. In interpreting the data in these figures it must be noted that the negative values obtained for nitrates under limed conditions are the result of deduction of appropriate check samples. The theory advanced for approximately equal nitrogen recovery under both limed and unlimed conditions despite the difference in nitrification is that plants were absorbing ammonia sufficient to balance the total nitrogen uptake. This theory is supported by the data in table 11, which shows the pH of the soil after 12 weeks of nitrification. The pH for limed and unlimed soil was practically the same at about 6.3. These data indicate that ammonia was produced and consequently raised the pH of the unlimed soil. Other data in this table supporting the theory of uptake of ammonia from 9520 is shown by the pH of the unlimed soil in the greenhouse pot tests. The pH of 5.4 under unlimed conditions indicates that the ammonia was largely taken up by the plants and therefore the soil pH was not raised. The total yields from this material were essentially the same under limed and unlimed conditions which furnishes further evidence of ammonia uptake. Some apparent toxicity possibly due to ammonia or its secondary effect was observed in the greenhouse pot tests but it did not appear to affect the yield.

From the results obtained with this material it appears that under greenhouse conditions slightly higher nitrogen recovery may be

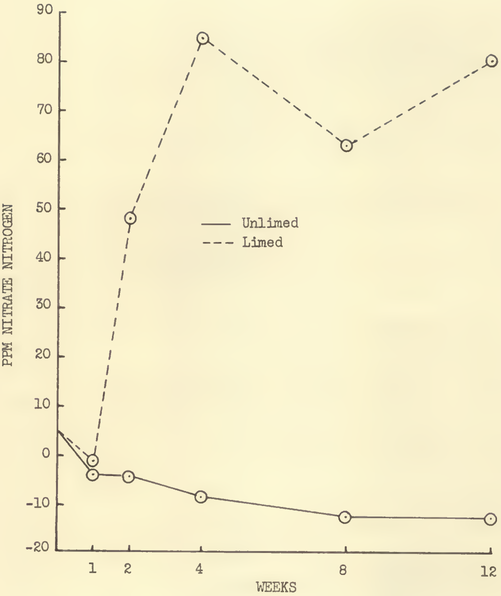

Figure 12--Nitrification of source 9520. Series 1.

Hexamethylenetetramine phosphate.
All of nitrogen water-soluble.

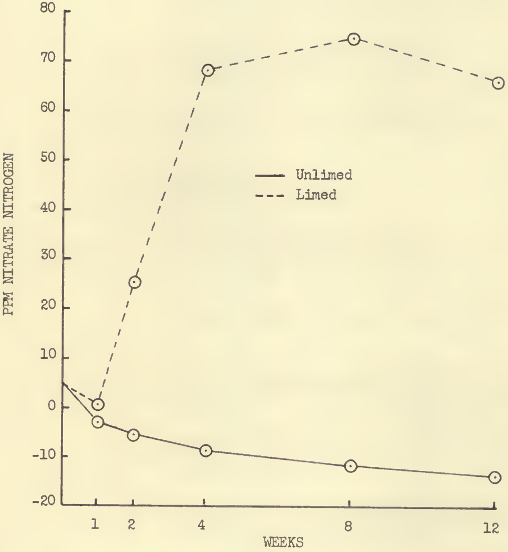

Figure 13--Nitrification of source 9520. Series 2.

Hexamethylenetetramine phosphate.
All of nitrogen water-soluble.

Table 11--Final pH values of Lakeland fine sand (initial pH 5.6) after various treatments

N Source	Nitrification Studies[a]		Greenhouse Pot Tests[b]	
	Series 1	Series 3	Series 1	Series 2
9829	4.5	---	5.0	5.1
9829 + lime	6.1	---	---	6.1
9830	4.4	---	5.0	5.3
9830 + lime	6.2	---	---	6.3
9830-W	4.4	---	5.0	5.3
9830-W + lime	6.2	---	---	6.2
9831	4.1	---	5.3	5.1
9831 + lime	6.1	---	---	6.1
9831-W	4.5	---	5.3	5.3
9831-W + lime	6.4	---	---	6.2
9832	4.3	---	5.1	5.2
9832 + lime	6.2	---	---	6.2
9520	6.4	---	5.1	5.4
9520 + lime	6.2	---	---	6.2
9538	4.7	---	5.2	5.3
9538 + lime	6.2	---	---	6.1
9537	4.3	---	5.2	---
9537 + lime	6.3	---	---	---
9539	4.3	---	5.2	---
9539 + lime	6.2	---	---	---
9900 + lime	---	---	---	6.3
9901 + lime	---	---	---	6.2
9913 + lime	---	---	---	6.2
9830-W[c]	---	---	---	5.4
9830-W[c] + lime	---	---	---	6.0

[a] 100 parts nitrogen per million parts soil.

[b] 100 pounds nitrogen per acre.

[c] 1,000 pounds nitrogen per acre.

Table 11--(continued)

N Source	Nitrification Studies[a]		Greenhouse Pot Tests[b]	
	Series 1	Series 3	Series 1	Series 2
7102	---	4.5	---	---
7102 + lime	---	6.6	---	6.2
7102-W	---	4.6	---	---
7102-W + lime	---	6.9	---	6.3
7105	---	4.5	---	---
7105 + lime	---	6.6	---	6.3
7105-W	---	4.6	---	---
7105-W + lime	---	6.8	---	6.2
7108	---	4.4	---	---
7108 + lime	---	6.6	---	6.3
7108-W	---	4.7	---	---
7108-W + lime	---	6.8	---	6.3
Urea	4.5	4.4	---	---
Urea + lime	6.2	6.6	---	---
$Ca(NO_3)_2$	---	4.7	---	---
$Ca(NO_3)_2$ + lime	---	6.8	---	---
Check	4.7	5.1	5.2	5.4
Check + lime	6.5	7.0	---	6.4

[a] 100 parts nitrogen per million parts soil.

[b] 100 pounds nitrogen per acre.

[c] 1,000 pounds nitrogen per acre.

expected from this material than from soluble sources of nitrogen such as those contained in 9829. The nitrogen uptake distribution appears to be less desirable than from 9829.

Nitrogen source 9537

This material was a fertilizer grade of methylenediurea and contained 41.3 percent total nitrogen and 10.85 percent water-insoluble nitrogen. It was included in the first series of greenhouse pot tests but not in the second series.

The data on this material (table 12) show that the total nitrogen recovered was practically equal to that from 9829. Also, the nitrogen uptake distribution was very similar. The yield data (table 13) show no important differences between the two materials.

Nitrate production from 9537 (figure 14), under unlimed soil conditions, is similar to that from urea (figure 9). However, under limed soil conditions nitrate production was about 20 percent less than from urea. The results obtained with this material (9537) therefore show that nitrogen recovery and yield is very similar to 9829.

Nitrogen source 9538

This material was fairly pure methylenediurea and contained 41.9 percent total nitrogen and 0.55 percent water-insoluble nitrogen.

The nitrogen recovery (table 12), yield, and nitrogen uptake distribution from this material was essentially the same as that from 9537 and 9829, in both of which the nitrogen is very rapidly available.

Table 12--Nitrogen recovery by oats and millet from various nitrogen sources when applied at the rates of 50, 100, and 200 pounds of nitrogen per acre to Lakeland fine sand in greenhouse pot tests. Series 1.

		Percent of Applied Nitrogen Recovered[a]				
N Source	N Rate (lbs/A)	1st oat clipping (56 days)	2nd oat clipping (38 days)	Oat roots	Millet (62 days)	Total
	50	56.8	5.7	5.5	0.0	68.0
9829	100	50.3	11.9	4.8	3.4	70.3
	200	41.2	13.2	6.8	8.7	69.9
	50	30.7	6.0	3.3	0.9	41.0
9830	100	33.3	7.6	5.4	1.0	47.0
	200	31.8	4.7	6.2	3.8	46.6
	50	10.4	6.7	6.8	4.9	27.7
9830-W	100	10.5	5.9	1.0	7.1	24.5
	200	10.0	6.0	2.9	11.3	30.1
	50	31.6	8.1	7.7	0.0	44.9
9831	100	33.4	6.8	4.7	3.5	48.5
	200	32.8	8.3	5.9	4.9	51.9
	50	5.4	6.9	5.4	2.4	20.1
9831-W	100	5.3	2.9	8.7	5.4	22.2
	200	5.4	3.1	1.4	3.4	13.3
	50	22.8	6.7	7.3	5.0	41.8
9832	100	24.3	7.3	4.2	4.0	39.9
	200	24.0	8.6	3.7	6.2	42.5
9520	100	36.9	18.5	0.6	6.7	62.2
9537	100	48.6	14.2	2.7	1.6	66.7
9538	100	51.8	13.2	5.6	1.6	72.3
9539	100	34.6	6.9	0.8	0.8	43.1

[a] Average of 3 replicates.

Table 13--Yield of oats and millet from various sources when applied at the rates of 50, 100, and 200 pounds of nitrogen per acre to Lakeland fine sand in greenhouse pot tests. Series 1.

		Yield in Grams per Pot (Average of 3 Replicates)				
N Source	N Rate (lbs./A)	1st oat clipping (56 days)	2nd oat clipping (38 days)	Oat roots	Millet (62 days)	Total
9829	50	8.6	2.9	7.9	4.1	23.5
	100	9.1	4.4	7.4	6.0	26.9
	200	9.9	5.1	7.0	10.0	32.0
9830	50	7.0	2.7	6.6	4.6	20.9
	100	8.6	3.7	8.1	4.8	25.2
	200	10.2	3.9	8.5	7.2	29.8
9830-W	50	4.8	2.7	7.6	5.8	20.9
	100	5.8	3.9	7.9	7.4	25.0
	200	7.3	3.7	8.3	12.1	31.4
9831	50	6.7	3.2	8.6	4.1	22.6
	100	8.4	3.8	6.9	6.2	25.3
	200	10.4	4.8	8.2	7.8	31.2
9831-W	50	4.4	2.5	8.3	5.1	20.3
	100	4.7	2.4	9.2	6.6	22.9
	200	5.8	2.9	7.7	7.2	23.6
9832	50	6.4	2.7	10.0	5.3	24.4
	100	7.5	3.1	7.0	6.0	23.6
	200	9.6	4.2	6.9	8.7	29.4
9520	100	5.9	4.3	4.1	7.5	21.8
9537	100	8.4	4.7	6.1	5.2	24.4
9538	100	8.5	4.6	7.1	5.5	25.7
9539	100	6.8	3.3	6.9	4.8	21.8
Check[a]	0	3.7	1.8	7.6	4.6	17.7

[a] Average of 6 replicates.

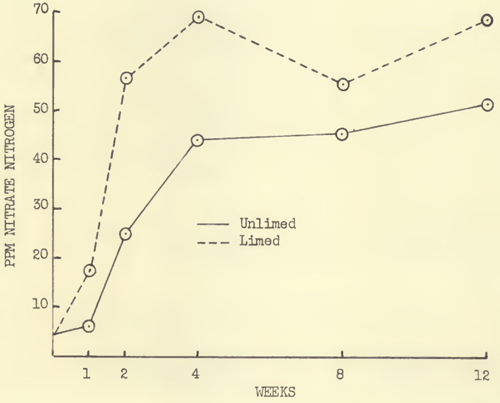

Figure 14--Nitrification of source 9537. Series 1.

Methylenediurea (fertilizer grade)
26.2 percent of nitrogen water-soluble.

The nitrification of this material (9538) under limed soil conditions (figure 15) was about 10 percent greater than 9537, but almost identical under unlimed soil conditions. This may be due to the fact that about 25 percent of the nitrogen in 9537 was water-insoluble, whereas in 9538 only about 1.3 percent of the nitrogen was water-insoluble.

Nitrogen source 9539

The composition of this material was not specified by the supplier, but it contained 20.9 percent nitrogen, all of which was water-soluble.

Total nitrogen recovery from 9539 (table 12) was about 30 percent less than from 9829, but the nitrogen recovery distribution was essentially the same, both furnishing much of their nitrogen in the early stages of plant growth thereby leaving very little nitrogen for later plant growth.

The nitrification of this material (figure 16) was about 10 percent less than 9538 under both limed and unlimed soil conditions.

Nitrogen source 7102

This material was formulated (table 3) to produce a product of low nitrogen solubility. It contained 14.37 percent nitrogen of which 61.9 percent was water-insoluble leaving 38.1 percent water-soluble. The water-insoluble portion was produced by the use of N-dure in the formulation.

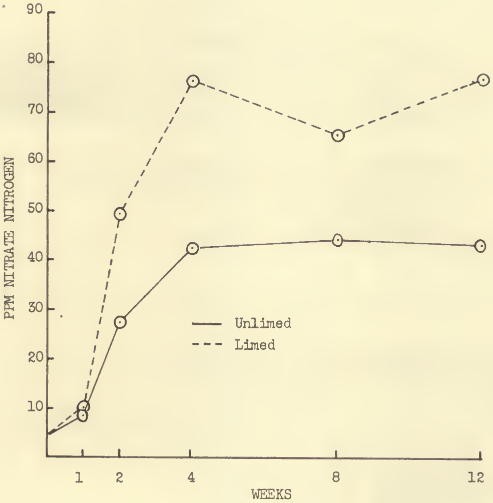

Figure 15--Nitrification of source 9538. Series 1.

Methylenediurea (fairly pure)
1.3 percent of nitrogen water-insoluble.

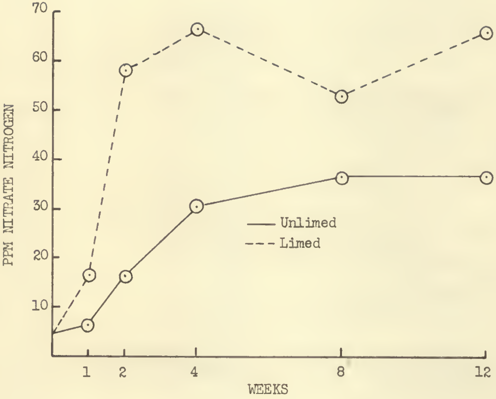

Figure 16--Nitrification of source 9539. Series 1

A highly water-soluble product of unspecified composition.

It will be noted in table 9 that the total nitrogen recovery was 33.9 percent or about one-half that from the standard soluble source (9829). Approximately three times as much nitrogen was recovered by the first clipping of oats as the second clipping. The net total nitrogen in the roots was approximately the same as in the second oat clipping, but the millet recovered only about one-twentieth as much as the second oat clipping.

The nitrification curve (figure 17) shows greater nitrate production from this material under limed conditions than under unlimed conditions for the first 8 weeks but in the 8 to 12 week period this condition had reversed.

The total yield data (table 10) show no significant difference between this material and the standard soluble source (9829). Yields gradually decreased from the first clipping of oats to the millet, the millet yield being only about 60 percent of the first yield of oats.

The results obtained with this material show that even though the nitrogen it contains is more slowly available than the nitrogen in 9829, the nitrogen uptake distribution leaves much to be desired.

Nitrogen source 7102-W

This material was the water-insoluble fraction of 7102 and contained only insoluble nitrogen produced by the use of N-dure.

Table 9 shows that the total nitrogen recovery from this material was 19.7 percent as compared to 33.9 percent from 7102, or about 58 percent as much. Also, each individual recovery was less. The nitrogen uptake distribution was considerably improved over 7102. Of the

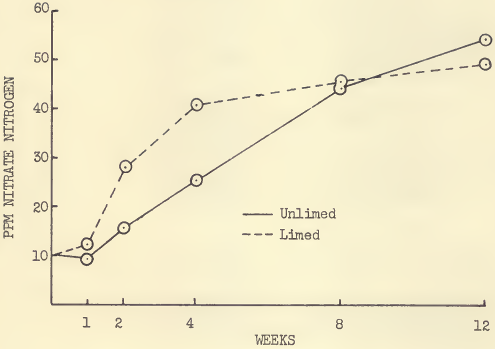

Figure 17--Nitrification of source 7102. Series 3.

61.9 percent of nitrogen water-insoluble from N-dure.

net total nitrogen absorbed about 37 percent was recovered by the first clipping of oats, 17 percent by the second, 30 percent was in the roots, and 15 percent in the millet. The first oat clipping recovered about twice as much nitrogen as the second as compared to three times as much for 7102.

The total yield from this material (table 10) was very little different from 7102. However, it is of interest to note the difference in yield distribution. The first oat clipping was 7 percent less, the second 6 percent less, but the millet was 40 percent more and statistically significant. This fact furnishes further evidence of the slower availability of the nitrogen in this material.

The nitrification curve for this material (figure 18) shows that nitrate production for the first four weeks was essentially the same under limed and unlimed conditions. During the 4 to 12 weeks period, nitrate production was greater under unlimed conditions. Nitrate production under limed conditions was about 15 percent less than from 7102.

The data on this material indicate that the nitrogen uptake distribution is a decided improvement over 7102, but still not ideal.

Nitrogen source 7105

The formulation of this material (table 3) was designed to produce a product of medium nitrogen solubility. It contained 14.07 percent total nitrogen of which 62.7 percent was water-insoluble.

The total nitrogen recovery from this material (table 9) was 45.7 percent as compared to 33.9 percent for 7102. However, the nitrogen

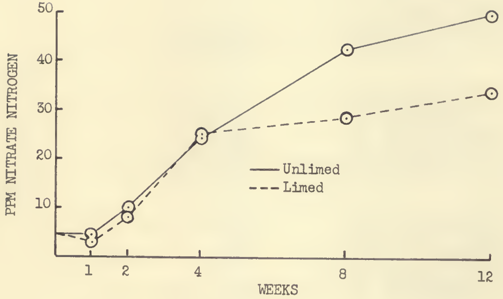

Figure 18--Nitrification of source 7102-W. Series 3.

All of nitrogen water-insoluble from N-dure.

uptake distribution was essentially the same as 7102.

The yield data (table 10) show that the yield of both clippings of oats, oat roots, and millet were higher than from 7102, but these differences were small and were not statistically significant.

The nitrification of this material (figure 19) was very similar to 7102, nitrate production being greater under limed conditions during the first 8 weeks after which the reverse was true.

These data point out the higher availability of the nitrogen in this material as compared to 7102. Of course, the nitrogen was more slowly available than from the standard soluble source (9829), but the nitrogen uptake distribution was not favorable.

Nitrogen source 7105-W

This source represents the water-insoluble fraction of 7105 and therefore contains water-insoluble nitrogen produced only by N-dure.

The total nitrogen recovery from this material (table 9) was 28.1 percent, or roughly one-third that of the standard soluble source (9829). It was about 10 percent more than from 7102-W, or slightly more than one-half that from 7105. The nitrogen uptake distribution appears to be good. Of the net total nitrogen absorbed by the crops, about 30 percent was recovered by the first clipping of oats, 24 percent by the second clipping, 35 percent by the oat roots, and 11 percent by the millet. This distribution was excellent for oats but the millet recovered only about one-half as much as the second clipping of oats.

The data obtained on recovery distribution for this material when applied at the rate of 100 pounds of nitrogen per acre as compared

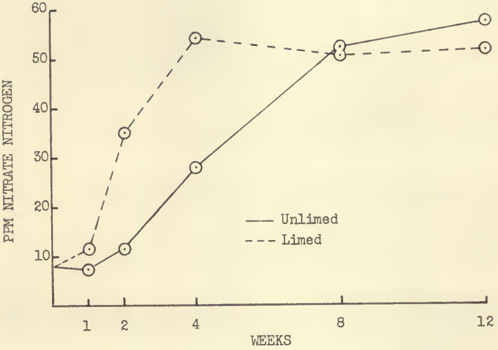

Figure 19--Nitrification of source 7105. Series 3.

62.7 percent of nitrogen water-insoluble
from N-dure.

to those obtained on 9830-W at the 100 pound and 1,000 pound rates, indicate that this material (7105-W) may prove to be as good or better than 9830-W when applied at a high rate.

The total yields (table 10) from 7105-W were essentially the same as from the standard soluble source (9829). Slightly higher nitrate production (figure 20) was obtained from this material (7105-W) than from 7102-W, the majority of this difference occurring after the fourth week.

The most important consideration with this material is the very favorable nitrogen uptake distribution obtained.

Nitrogen source 7108

The formulation (table 3) used in the preparation of this material was designed to produce a product having a relatively low level of insoluble nitrogen. The product contained 15 percent total nitrogen of which only 18.5 percent was water-insoluble.

Total nitrogen recovery from this material (table 9) was relatively quite high, being only about 6 percent less than from the standard soluble source (9829). The first clipping of oats recovered approximately the same percentage of nitrogen from both materials (7108 and 9829); but the second clipping of oats recovered 24.8 percent from 9829 as compared to 18.2 percent from 7108. This fact points out the rapidity with which the nitrogen in the standard source (9829) becomes available.

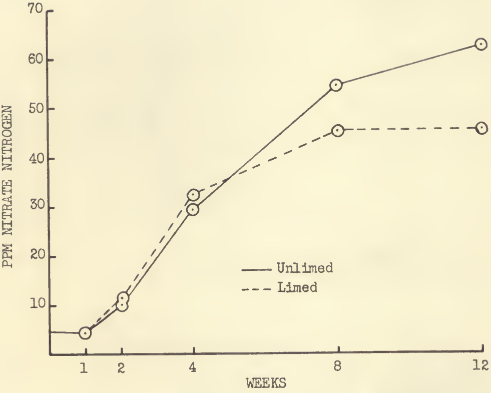

Figure 20--Nitrification of source 7105-W. Series 3.

All of nitrogen water-insoluble from N-dure.

The nitrogen uptake distribution from this material (7108) was very poor. Of the net total nitrogen absorbed about 60 percent was recovered by the first clipping of oats, 26 percent by the second clipping, 11 percent in the oat roots, and only 2 percent by the millet.

The total yield from this material (table 10) was practically identical to the yield from the standard soluble source. The total nitrate production from this material (figure 21) was quite high, approximating that from urea (figure 22). The rate of nitrification was higher under limed soil conditions than under unlimed conditions during the first 4 weeks, but at the end of the 12 weeks period total nitrate production was essentially equal.

It is obvious from the results obtained with this material that the nitrogen it contains is too rapidly available to be considered of much value as a slowly available source.

Nitrogen source 7108-W

This material was the water-insoluble fraction of 7108 and contained water-insoluble nitrogen produced only by N-dure.

The total nitrogen recovery from this material (table 9) was 37.4 percent or approximately one-half that from the standard soluble source (9829), slightly more than one-half that from 7108, and about 10 percent greater than from 7105-W. Of the net total nitrogen absorbed by the crops, approximately 50 percent was recovered by the first clipping of oats, 21 percent by the second clipping, 21 percent by the roots, and 9 percent by the millet. This high percentage recovery by the first

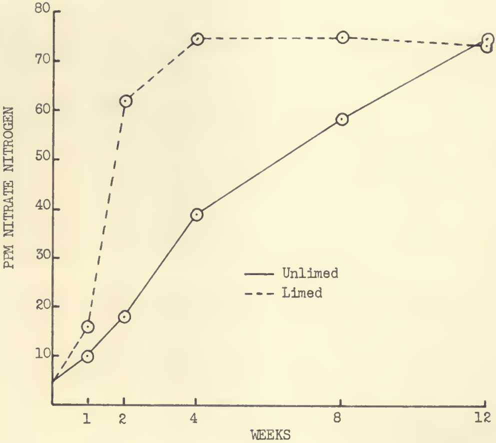

Figure 21--Nitrification of source 7108. Series 3.

18.5 percent of nitrogen water-insoluble from N-dure.

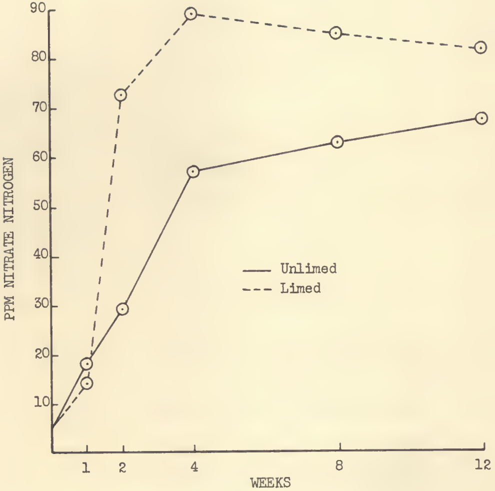

Figure 22--Nitrification of urea. Series 3.

oat clipping and low percentage for the millet is considered to be unsatisfactory for a slowly soluble source of nitrogen.

The total yield of oats and millet with this material (table 10) is essentially the same as with the standard soluble source (9829). The rate of nitrification of this material (figure 23) under unlimed conditions was practically identical to that of 7108 (figure 21) throughout the 12 weeks period. Under limed conditions the rate was much less than that of 7108 during the first 4 weeks but in the 4 to 12 weeks period their rates were practically the same. These results indicate that the higher rate of nitrification in 7108 during the initial 4 weeks period was due to the easily nitrifiable material (urea) it contained.

Nitrogen source 9900

This material was a laboratory sample of low solubility ureaform rather than a commercial product. It contained 37.51 percent total nitrogen and 35.90 percent water-insoluble nitrogen. Therefore 95.7 percent of the total nitrogen it contained was water-insoluble.

Total nitrogen recovery from this material (table 9) was 46.9 percent or about 62 percent of that recovered from the standard soluble source (9829). This recovery also approximated that from 7105, 9830, and 9831 under the same conditions. The nitrogen uptake distribution was also very similar to 7105. Of the total nitrogen recovered, about 58 percent was in the first clipping of oats, 22 percent in the second clipping, 14 percent in the oat roots, and 5 percent in the millet. This recovery by the first oat clipping was quite high, being about

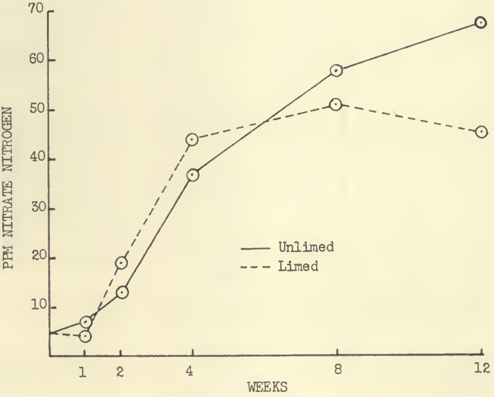

Figure 23--Nitrification of source 7108-W. Series 3.

All of nitrogen water-insoluble from N-dure.

5 percent higher than that recovered from 9829 under the same conditions. Therefore, the nitrogen uptake distribution from this material was not very favorable. Total yield (table 10) was essentially the same as from the standard soluble source (9829).

The nitrification curve (figure 24) for this material shows that at the end of 4 weeks the nitrates were greater under limed conditions, but the reverse was true at the end of 8 weeks, with an even greater difference at the end of 12 weeks.

Nitrogen source 9901

This material was the chemical compound, trimethylenetetraurea. It contained 39.38 percent total nitrogen and 38.16 percent water-insoluble nitrogen. Therefore, 96.9 percent of the nitrogen it contained was water-insoluble.

As noted in table 10, the total nitrogen recovery from this compound was surprisingly high considering the fact that approximately 97 percent of the nitrogen it contained was water-insoluble, the recovery being almost equal to that from the standard soluble source (9829). These data point out that the portion of the total nitrogen in a material that is water-insoluble is not necessarily inversely related to percent nitrogen recovery. The recovery by the first clipping of oats was 39.6 percent, and was essentially identical to that recovered from the soluble source. The recovery by the second clipping was about 10 percent less but the recovery by the oat roots was about 5 percent more than from the soluble source. The recovery by the millet

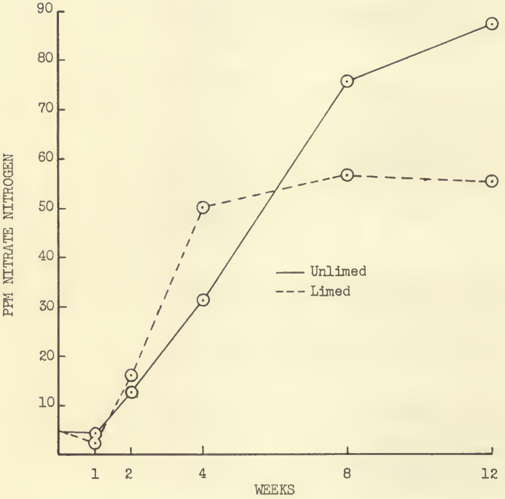

Figure 24--Nitrification of source 9900. Series 2.

95.7 percent of nitrogen water-insoluble from ureaform (Nitroform).

was very low, being only 2 percent. The nitrogen uptake distribution from this compound was very similar to that of 7102 and 7105 under the same conditions. However, percent total nitrogen recovery from 7102 and 7105 were much less.

Total yield from this compound (table 10) at 100 pounds nitrogen per acre in limed soil was higher than from any other material under the same conditions. The yield was significantly higher than from the standard soluble source.

The nitrification of this compound is shown in figure 25. Under both limed and unlimed soil conditions, the rate of nitrification of the compound was quite rapid during the first 4 weeks, being more rapid under limed conditions. After 4 weeks the rate was low and fairly constant. The total nitrate nitrogen production was higher under limed conditions. The nitrification of this compound was very similar to that of urea (figure 26) under unlimed conditions, but under limed conditions total nitrate production was about 20 percent less.

Nitrogen source 9913

This source was the chemical compound, dimethylenetriurea. It contained 40.2 percent nitrogen and 8.3 percent water-insoluble nitrogen. Accordingly, 20.6 percent of the total nitrogen it contained was water-insoluble.

As shown in table 9, the total nitrogen recovered from this compound was 75 percent, and equalled that of the standard soluble source (9829).

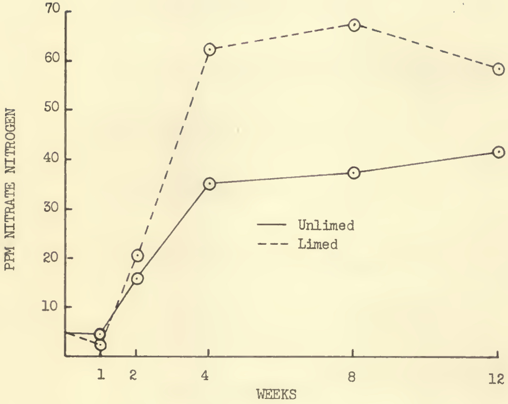

Figure 25--Nitrification of source 9901. Series 2.

Trimethylenetetraurea
96.9 percent of nitrogen water-insoluble.

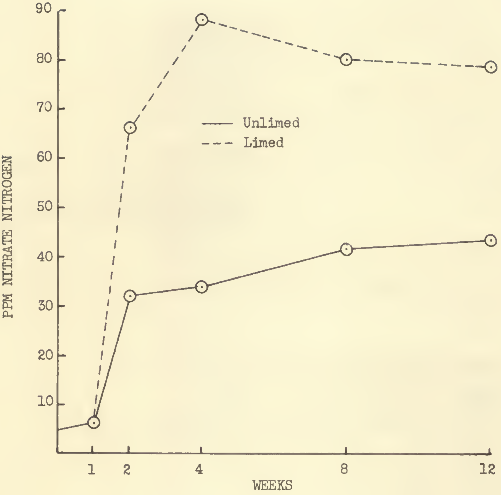

Figure 26--Nitrification of urea. Series 2.

The first oat clipping recovered about 66 percent of the net total nitrogen absorbed by the crops; the second clipping, 21 percent; the oat roots, 12 percent; and the millet, only about 1 percent. It will be noted that the first oat clipping recovered more nitrogen from this compound than was recovered under the same conditions from the standard soluble source (9829). Therefore, the nitrogen uptake distribution from this compound was even less favorable than that from the standard soluble source.

Figure 27 shows the nitrification of this compound. It will be noted that this curve is very similar to that of urea (figure 26). During the first 2 weeks the rate of nitrification was slightly less than that of urea, but at the end of 12 weeks the total nitrate production was practically the same.

The total yield of oats and millet from this compound was slightly higher than from the standard soluble source but was not statistically significant.

The relative percentages of nitrogen recovery from the various materials are shown in figure 28 (Appendix).

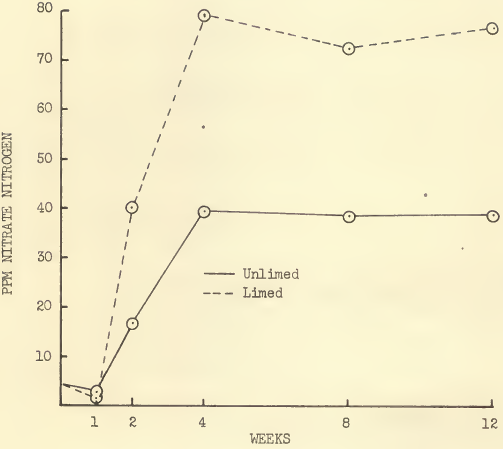

Figure 27--Nitrification of source 9913. Series 2.

Dimethylenetriurea
20.6 percent of nitrogen water-insoluble.

SUMMARY AND CONCLUSIONS

A series of laboratory and greenhouse experiments were conducted to study the availability of the nitrogen contained in certain condensation products of the reaction of urea with formaldehyde. Special emphasis was placed on the availability of the water-insoluble nitrogen produced by the use of N-dure solution (59 percent formaldehyde and 26 percent urea) in the manufacture of 14-7-7 fertilizers. The soil used in this study was a Lakeland fine sand having an initial pH of 5.6 and containing 0.06 percent total nitrogen and 4.8 parts per million nitrate nitrogen at the time of use. The rate of nitrogen applied from the various sources generally was 100 pounds per acre. The crops used were oats and millet. The oats were clipped after 42 days growth and again 31 days later. Oat roots were harvested and then the pots planted to millet which was clipped after 48 days growth. The oat clippings, the oat roots, and the millet were analyzed separately for nitrogen.

The criteria used to determine the nitrogen availability were as follows: (1) the nitrification of these products in Lakeland fine sand during 12 weeks in the laboratory under controlled temperature and moisture conditions; and (2) the nitrogen uptake from these products by oats and millet in greenhouse pot tests.

In the greenhouse, oats, oat roots, and millet recovered a total of 71 percent of the applied nitrogen from a soluble source mixture containing ammonia, ammonium nitrate, and ammonium sulfate under unlimed soil conditions, and 75 percent when the soil was limed with dolomite at the rate of 2,000 pounds per 2,000,000 pounds of soil. Of the net total nitrogen absorbed by oats and millet, about 50 percent was recovered by the oats in the first 42 days of growth and about 33 percent in the next 31 days. Nitrification of this nitrogen source in the laboratory was greater in limed soil.

Approximately 44 percent total nitrogen recovery was obtained from a fertilizer material (14-7-7) having 46.3 percent of its nitrogen as water-insoluble, produced by N-dure, and the remainder soluble from inorganic sources and urea. Net total nitrogen absorption was essentially the same from limed and unlimed soil. The first clipping represented 65 percent of the total nitrogen absorbed by the crops from the partially water-insoluble mixture. This compares to 55 percent of the total absorbed nitrogen that appeared in the first clipping from the standard soluble source. However, the latter represented a higher total absorption by the first clipping from the soluble source.

The total nitrogen recovered from a material containing only water-insoluble nitrogen produced by N-dure was only about 20 percent as compared to 75 percent recovery from the standard soluble source by the oats and millet. Oat and millet clippings recovered a slightly higher percentage of nitrogen from this water-insoluble material under unlimed soil conditions than under limed conditions. The reverse was true with oat roots. The first oat clipping recovered about one-fifth that recovered from the standard soluble source. Recovery of residual nitrogen by millet was about three times that from the standard soluble source apparently because of earlier depletion of soluble nitrogen by the oat roots. Of the net total nitrogen absorbed, 35 to 44 percent was recovered by the first oat clipping, 14 to 18 percent by the second oat clipping, and 16 to 18 percent by the millet. Nitrification of this material was greater in unlimed soil than limed soil.

This material (water-insoluble nitrogen produced by N-dure) was also applied at the rate of 1,000 pounds of nitrogen per acre. The total nitrogen recovered was approximately 25 percent of that applied. Of the total nitrogen recovered, about 35 percent was recovered by each of the oat clippings and about 20 percent by the millet. The remaining 10 percent was in the oat roots. This was the only material applied at the 1,000 pound rate; however, the nitrogen uptake distribution was the most favorable of all treatments.

The total nitrogen recovery from three materials containing only water-insoluble nitrogen produced by N-dure increased with increasing urea to formaldehyde mole ratios.

Total nitrogen recovery from a material containing only water-insoluble nitrogen from ureaform (Nitroform) was about one-tenth that from the standard soluble source or about one-third that from a material containing only water-insoluble nitrogen produced by N-dure. Oat and millet clippings recovered a higher percentage of nitrogen from this material in unlimed soil than from the same in limed soil. The reverse was true with oat roots.

Total nitrogen recovery from hexamethylenetetramine phosphate was about 10 percent higher than from the standard soluble source. Of the net total nitrogen absorbed by the crops, about 65 percent was recovered in the first oat clipping and about 25 percent in the second oat clipping. Nitrification of this material in limed soil was very high and approached that of urea, but in the unlimed soil nitrate production was less than that in the untreated soil.

Total nitrogen recovery from methylenediurea was slightly higher than from the standard soluble source. Of the net total nitrogen absorbed, about 63 percent was recovered in the first clipping of oats or about 10 percent more than from the standard soluble source. The recovery by the second oat clipping was about 10 percent less than from the standard soluble source. The nitrification of this compound (methylenediurea) was similar to that of urea.

The recovery of nitrogen from dimethylenetriurea was essentially the same as for the standard soluble source. However, of the net total nitrogen taken up by the crops, about 66 percent was recovered by the first oat clipping as compared to about 53 percent from the standard source. Nitrification of this compound was practically the same as urea.

Total nitrogen recovery from trimethylenetetraurea was slightly less than from the standard soluble source. Also the nitrogen recovery distribution was essentially the same except that the recovery by the second oat clipping was about 10 percent less than from the standard soluble source. Even though 97 percent of the nitrogen in this compound (trimethylenetetraurea) was water-insoluble, its insolubility did not affect the total nitrogen recovery appreciably.

The results and conclusions of this investigation may be summarized as follows:

1. The nitrogen contained in a standard soluble source derived from ammonia, ammonium nitrate, and ammonium sulfate was very readily available. More than one-half of the nitrogen taken up by the crops was recovered in the first 42 days by oats.
2. In treatments using only water-insoluble nitrogen produced by N-dure at 100 pounds nitrogen per acre the availability of the nitrogen increased with an increase in the urea to formaldehyde mole ratio.
3. When water-insoluble nitrogen produced by N-dure was applied at the rate of 1,000 pounds of nitrogen per acre it gave a very favorable nitrogen uptake distribution for the first two oat clippings. Total yields were about twice those obtained from the standard soluble nitrogen source, although maximum yields for the soluble source appeared to occur when the nitrogen was applied at a rate less than 100 pounds of nitrogen per acre.
4. The nitrogen contained in hexamethylenetetramine phosphate appeared to be absorbed more readily than that in the standard soluble source.
5. The availability of the nitrogen contained in methylenediurea, dimethylenetriurea, and trimethylenetetraurea was

quite high. The availability was not greatly different from the soluble source. However, the availability of the nitrogen in these compounds appeared to be in the following decreasing order: methylenediurea, dimethylenetriurea, trimethylenetetraurea. The nitrogen uptake distribution from trimethylenetetraurea appeared to be more favorable than from methylenediurea.

APPENDIX

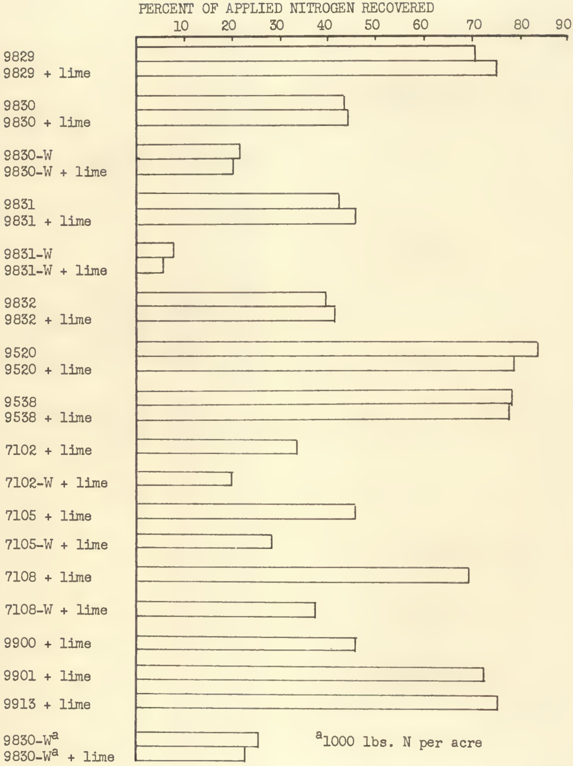

Figure 28--Total nitrogen recovery by oats and millet from various sources applied at the rate of 100 pounds of nitrogen per acre (except as noted). Series 2.

Table 14--The analysis of variance of the yield of the first clipping of oats from greenhouse pot tests. Series 2.

Source of variation	Degrees of freedom	Sum of squares	Mean square	F
Total	74	52.69	0.7120	
Treatments	24	48.06	2.0025	21.63**
Error	50	4.63	0.0926	

**Significant at the one percent level.

Table 15--The analysis of variance of the yield of the second clipping of oats from greenhouse pot tests. Series 2.

Source of variation	Degrees of freedom	Sum of squares	Mean square	F
Total	74	49.78	0.7270	
Treatments	24	44.15	1.8396	16.34 **
Error	50	5.63	0.1126	

** Significant at the one percent level.

Table 16--The analysis of variance of the yield of millet from greenhouse pot tests. Series 2.

Source of variation	Degrees of freedom	Sum of squares	Mean square	F
Total	74	36.69	0.4958	
Treatments	24	25.77	1.0738	4.92**
Error	50	10.92	0.2184	

**Significant at the one percent level.

Table 17--The analysis of variance of the total yield of oats and millet from greenhouse pot tests. Series 2.

Source of variation	Degrees of freedom	Sum of squares	Mean square	F
Total	74	467.0	6.311	
Treatments	24	303.3	12.638	3.86**
Error	50	163.7	3.274	

**Significant at the one percent level.

Table 18--The analysis of variance of nitrogen recovery by the first clipping of oats from greenhouse pot tests. Series 2.

Source of variation	Degrees of freedom	Sum of squares	Mean square	F
Total	74	18,533.86	250.45	
Treatments	24	18,209.02	758.71	116.72**
Error	50	324.84	6.50	

**Significant at the one percent level.

Table 19--The analysis of variance of nitrogen recovery by the second clipping of oats from greenhouse pot tests. Series 2.

Source of variation	Degrees of freedom	Sum of squares	Mean square	F
Total	74	4,521.00	61.09	
Treatments	24	4,019.03	167.46	16.68**
Error	50	501.97	10.04	

**Significant at the one percent level.

Table 20--The analysis of variance of nitrogen recovery by millet from greenhouse pot tests. Series 2.

Source of variation	Degrees of freedom	Sum of squares	Mean square	F
Total	74	120.50	1.628	
Treatments	24	82.03	3.418	4.44**
Error	50	38.47	0.769	

**Significant at the one percent level.

Table 21--The analysis of variance of the total nitrogen recovery of oats and millet from greenhouse pot tests. Series 2.

Source of variation	Degrees of freedom	Sum of squares	Mean square	F
Total	74	41,602.05	562.19	
Treatments	24	40,654.58	1,693.94	89.39**
Error	50	947.47	18.95	

**Significant at the one percent level.

Table 22--Test of significance for the effect of nitrogen sources and lime on yield of first clipping of oats from greenhouse pot tests. Series 2.

Treatment No.	Mean yield					
13	6.3	│				
25	6.1	│				
24	6.0	│				
15	5.8	│	│			
16	5.7	│	│			
14	5.7	│	│			
21	5.2		│	│		
7	5.0	│		│		
2	5.0	│		│		
11	4.9	│	│	│		
3	4.9	│	│	│		
1	4.9	│	│	│		
23	4.8	│	│	│		
19	4.7	│	│	│		
12	4.7	│	│	│		
4	4.6	│	│	│	│	
8	4.5	│	│		│	│
22	4.3		│	│	│	│
17	4.3		│	│	│	│
18	4.0	│		│	│	│
5	3.9	│		│		│
6	3.7	│		│		
20	3.7	│		│		
7	3.6	│				
10	3.4	│				

Notes:

Any two means covered by the same vertical line are not significantly different. Any two not covered by the same vertical line are significantly different at the 5 percent level.

Table 23--Test of significance for the effect of nitrogen sources and lime on yield of second clipping of oats from greenhouse pot tests. Series 2.

Treatment No.	Mean yield						
1	5.0	|					
2	4.9	|					
16	4.6	|					
14	4.6	|					
21	4.5	|	|		|		
24	4.5	|	|		|		
25	4.4	|	|		|		
15	4.2		|		|		|
13	4.0	|	|		|		|
19	3.8	|		|	|	|	|
23	3.5	|		|		|	|
12	3.5	|		|		|	|
8	3.5	|		|		|	|
3	3.5	|		|	|	|	|
22	3.4	|		|	|	|	
11	3.4	|		|	|	|	
7	3.4	|		|	|	|	
20	3.3	|		|	|	|	
4	3.3	|		|	|	|	
17	3.2			|	|	|	
18	3.0	|		|	|		
5	2.7	|	|		|		
6	2.5	|	|				
10	2.3		|				
9	2.3		|				

Notes:

Any two means covered by the same vertical line are not significantly different. Any two not covered by the same vertical line are significantly different at the 5 percent level.

Table 24--Test of significance for the effect of nitrogen sources and lime on yield of millet from greenhouse pot tests. Series 2.

Treatment No.	Mean yield							
6	4.2	│						
22	4.1	│	│					
20	3.9	│	│	│				
18	3.8	│	│	│	│			
23	3.5	│	│	│	│	│		
5	3.3	│	│	│	│	│	│	
24	3.2		│	│	│	│	│	
21	3.2	│	│	│	│	│	│	
25	3.1	│		│	│	│	│	│
19	3.0	│	│	│	│	│	│	│
12	3.0	│	│	│	│	│	│	│
16	2.9	│	│		│	│	│	│
14	2.9	│	│		│	│	│	│
4	2.9	│	│		│	│	│	│
3	2.9	│	│		│	│	│	│
8	2.8	│	│			│	│	│
17	2.7	│	│			│	│	│
10	2.6	│	│				│	│
7	2.6	│	│				│	│
13	2.3	│	│					│
9	2.2		│					│
2	2.2		│					│
1	2.2		│					│
15	2.1		│					
11	1.2							

Notes:

Any two means covered by the same vertical line are not significantly different. Any two not covered by the same vertical line are significantly different at the 5 percent level.

Table 25--Test of significance for the effect of nitrogen sources and lime on total yield of oats and millet from greenhouse pot tests. Series 2.

Treatment No.	Mean yield						
24	24.2	│					
13	23.2	│	│				
12	22.3	│	│	│			
16	22.1	│	│	│	│		
25	21.7	│	│	│	│		
21	21.0	│	│	│	│	│	
15	20.6	│	│	│	│	│	│
20	20.4		│	│	│	│	│
14	20.4		│	│	│	│	│
22	20.3		│	│	│	│	│
23	19.9		│	│	│	│	│
2	19.8		│	│	│	│	│
11	19.7		│	│	│	│	│
19	19.6		│	│	│	│	│
18	19.5			│	│	│	│
7	19.4			│	│	│	│
6	19.4			│	│	│	│
3	19.4			│	│	│	│
8	19.0	│		│	│	│	│
1	18.6	│			│	│	│
4	18.5	│			│	│	│
17	17.6	│				│	│
5	17.3	│	│				│
10	16.2	│	│				
9	14.8		│				

Notes:

Any two means covered by the same vertical line are not significantly different. Any two not covered by the same vertical line are significantly different at the 5 percent level.

Table 26--Test of significance for the effect of nitrogen sources and lime on nitrogen recovery by first clipping of of oats from greenhouse pot tests. Series 2.

Treatment No.	Mean			
13	54.1			
25	49.6	│		
15	49.5	│		
14	49.3	│		
16	48.1	│		
21	41.5		│	
2	40.0		│	
24	39.6		│	
1	38.3		│	
7	29.6	│		
8	29.4	│		
4	28.5	│		
3	28.5	│		
23	27.4	│		
19	26.2	│	│	
11	22.9		│	│
12	19.9			│
17	19.9			│
22	18.5			│
5	9.5	│		
20	8.4	│	│	
18	7.4	│	│	
6	7.0	│	│	│
9	4.5		│	│
10	2.7			│

Notes:

Any two means covered by the same vertical line are not significantly different. Any two not covered by the same vertical line are significantly different at the 5 percent level.

Table 27--Test of significance for the effect of nitrogen sources and lime on nitrogen recovery by second clipping of oats from greenhouse pot tests. Series 2.

Treatment No.	Mean					
1	26.1	│				
2	24.8	│	│			
14	21.1	│	│	│		
16	20.6	│	│	│		
15	19.4		│	│		
21	18.2			│		
13	17.8			│		
25	16.1			│		
24	15.7			│		
23	10.4	│				
19	10.2	│				
8	9.2	│				
12	8.4	│	│			
22	7.9	│	│	│		
4	7.0	│	│	│		
17	7.0	│	│	│		
11	6.9	│	│	│		
20	6.7	│	│	│		
3	6.7	│	│	│		
7	6.4	│	│	│	│	
5	3.9		│	│	│	│
18	3.4			│	│	│
6	2.8			│	│	│
9	1.1				│	│
10	0.3					│

Notes:

Any two means covered by the same vertical line are not significantly different. Any two not covered by the same vertical line are significantly different at the 5 percent level.

Table 28--Test of significance for the effect of nitrogen sources and lime on nitrogen recovery by millet from greenhouse pot tests. Series 2.

Treatment No.	Mean					
5	3.9	│				
20	3.3	│	│			
22	3.2	│	│			
6	3.2	│	│			
18	3.0	│	│	│		
3	2.8	│	│	│	│	
23	2.3	│	│	│	│	│
7	2.0		│	│	│	│
11	1.9		│	│	│	│
9	1.4	│		│	│	│
24	1.3	│		│	│	│
21	1.3	│		│	│	│
1	1.2	│			│	│
19	1.1	│				│
14	1.1	│				│
13	1.1	│				│
8	1.1	│				│
15	1.0	│				│
12	1.0	│				│
4	0.8	│				│
25	0.7	│				│
17	0.4	│				│
16	0.4	│				│
10	0.4	│				│
2	0.0	│				

Notes:

Any two means covered by the same vertical line are not significantly different. Any two not covered by the same vertical line are significantly different at the 5 percent level.

Table 29--Test for significance for the effect of nitrogen sources and lime on total nitrogen recovery by oats and millet from greenhouse pot tests. Series 2.

Treatment No.	Mean				
13	83.4	|			
14	78.1	|	|		
15	77.9	|	|		
16	77.8	|	|		
25	75.3	|	|	|	
2	75.1		|	|	
24	72.2		|	|	
1	70.9		|	|	
21	69.0			|	
23	46.9	|			
19	45.7	|	|		
7	45.5	|	|		
4	44.4	|	|		
3	43.4	|	|		
7	42.4	|	|		
12	41.6	|	|	|	
11	39.1	|	|	|	
22	37.4		|	|	
17	33.9	|		|	
20	28.1	|	|		|
5	21.6		|		|
6	20.0				|
18	19.7				|
9	7.9	|			
10	5.9	|			

Notes:

Any two means covered by the same vertical line are not significantly different. Any two not covered by the same vertical line are significantly different at the 5 percent level.

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Franklin Leslie Long was born in Liberty County, Georgia, on July 22, 1918. He is the son of Ida Mae Cameron Long and the late Hilton Frank Long of Ludowici, Georgia. He was married to Lucy Bunce, daughter of Mr. and Mrs. James Arthur Bunce of Statesboro, Georgia in June, 1943.

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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of the committee. It was submitted to the Dean of the College of Agriculture and to the Graduate Council and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August 13, 1960

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